

L Number	Hits	Search Text	DB	Time stamp
273	1	water and (hydrogen adj peroxide) and molybdenum and (etch\$3 or remov\$3) and ((percentage or percent or ratio or "%") same (hydrogen adj peroxide))and (molybdenum same (etch\$3 or remov\$3))	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 11:21

PAT-NO: JP404084428A  
DOCUMENT-IDENTIFIER: JP 04084428 A  
TITLE: MANUFACTURE OF SEMICONDUCTOR DEVICE  
PUBN-DATE: March 17, 1992

INVENTOR-INFORMATION:  
NAME  
TAKAHASHI, SEIICHI

ASSIGNEE-INFORMATION:  
NAME COUNTRY  
NEC CORP N/A

APPL-NO: JP02199632  
APPL-DATE: July 27, 1990

INT-CL (IPC): H01L021/302, H01L027/04 , H01L027/092  
US-CL-CURRENT: 438/488

ABSTRACT:

PURPOSE: To obtain a high relative accuracy and an absolute accuracy in case a polycrystalline semiconductor layer is used for the formation of a resistance element by a method wherein parts, which are situated on the side surfaces of step parts on a semiconductor substrate, of the polycrystalline semiconductor layer are previously removed.

CONSTITUTION: An anisotropic dry etching is performed to remove an oxide film on the surface of a polycrystalline silicon layer. At this time, the

oxide film 109 on the side surfaces of parts, which cover gate electrodes, of the polycrystalline silicon layer is left. Subsequently, a thin film layer 110 consisting of transition metal element, such as tungsten, molybdenum or the like, or the like or a substance having a selection ratio with respect to etching with silicon oxide and polycrystalline silicon, such as tungsten, is selectively grown on the polycrystalline silicon layer. Then, after the film 109 is removed with a hydrofluoric acid, parts, which are situated on the side surfaces of the gate electrodes, of the polycrystalline silicon layer are removed using the mixed aqueous solution of a hydrofluoric acid, a nitric acid and an iodine-containing glacial acetic acid. Subsequently, after the tungsten thin film layer 109 is removed using the mixed solution of ammonia water and hydrogen peroxide water, a photoresist 111 is formed into a desired form by a photolithography technique and an anisotropic dry etching is performed using this photoresist 111 as a masking material to form a resistance element 112.

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US-PAT-NO: 5851303

DOCUMENT-IDENTIFIER: US 5851303 A

TITLE: Method for removing metal surface  
contaminants from  
silicon

----- KWIC -----

Abstract Text - ABTX (1):

A method for removing metal surface contaminants from silicon metalloid. The method comprises sequentially contacting the silicon with gaseous hydrogen fluoride and then with an aqueous solution comprising at least one-half weight percent hydrogen peroxide. The method is especially useful as a means for recovering metal surface contaminants on semiconductor grade silicon for analysis of surface contamination of the silicon by such metals. The method is useful for recovering copper from the surface of semiconductor grade silicon in an aqueous solution which can be analyzed directly to determine the amount of copper contamination of the surface of the silicon.

US Patent No. - PN (1):  
5851303

Application Filing Date - AD (1):  
19960502

TITLE - TI (1):

Method for removing metal surface contaminants from  
silicon



Brief Summary Text - BSTX (2):

The present invention is a method for removing metal surface contaminants from silicon metalloid. The method comprises sequentially contacting the silicon with gaseous hydrogen fluoride and then with an aqueous solution comprising at least one-half weight percent hydrogen peroxide. The method is especially useful as a means for recovering metal surface contaminants on semiconductor grade silicon for analysis of surface contamination of the silicon by such metals. The method is useful for recovering copper from the surface of semiconductor grade silicon in an aqueous solution which can be analyzed directly to determine the amount of copper contamination on the surface of the silicon.

Brief Summary Text - BSTX (3):

The production of high density integrated circuits requires wafers of monocrystalline silicon of high purity. Metal contaminants of the silicon including, among others, copper, gold, iron, cobalt, nickel, chromium, tantalum, zinc, tungsten, titanium, magnesium, molybdenum, and aluminum can be harmful to the production of such integrated circuits. These impurities, even in small amounts, may introduce defect sites in the semiconductor grade material which can ultimately result in degraded device performance and limited circuit density. Therefore to control the quality of silicon intended for use in the semiconductor industry, methods for cleaning silicon as well as accurate methods for determining metals contamination of the surface are desired.

Brief Summary Text - BSTX (4):

Methods for surface cleaning of silicon used in semiconductor devices are

well known in the art. Such methods are described in Iscoff (Editor), Semiconductor International, July, 1993, pages 58-63, and include a method typically referred to as the "RCA" method. The RCA method comprises cleaning the silicon with an aqueous  $\text{H}_2\text{O}_2$ - $\text{NH}_4\text{OH}$  and an aqueous  $\text{H}_2\text{O}_2$ -HCL mixture at 75.degree. C. to 80.degree. C. for 10 minutes. Burggraaf (Editor), Semiconductor International, October, 1990, pages 52 to 58, further discusses such cleaning techniques. Burggraaf states that although a HF-vapor process can remove native oxide layers, these processes cannot effectively remove metallic contaminants because most metals do not generate volatile species with appreciable vapor pressure. Burggraaf further states that an integral deionized water rinse following exposure to vapor-phase HF cleaning can remove soluble metallic species.

Brief Summary Text - BSTX (6):

Niwayama et al., JP (Heisei) 5-4811, describe the treatment of silicon with an aqueous solution of hydrogen fluoride and hydrogen peroxide. The solution comprises by volume one portion of a 50 weight percent aqueous solution of hydrogen fluoride, 0.03 to 4 portions of a 31 weight percent hydrogen peroxide solution, and one to ten portions of water.

Brief Summary Text - BSTX (7):

In a preferred embodiment of the present invention metal surface contaminants are recovered from semiconductor grade silicon in an aqueous solution, which is then analyzed by standard analytical techniques to quantify the amount of metal surface contamination of the semiconductor grade silicon. The present method offers an advantage over wet methods currently used in the

art for cleaning silicon metalloid by not requiring large volumes of aqueous hydrogen fluoride. Another advantage of the present method is the ability to remove metal oxides and metals bonded directly to silicon, such as copper, from the surface of the silicon. The present method allows for essentially quantitative recovery of metal surface contaminants, such as copper, in aqueous solution from the surface of semiconductor grade silicon, and thereby provides a convenient solution for analysis of the concentrations of the removed metals.

Brief Summary Text - BSTX (9):

The present invention is a method for removing metal surface contaminants from silicon metalloid. The method comprises sequentially contacting the silicon with gaseous hydrogen fluoride and then with an aqueous solution comprising at least one-half weight percent hydrogen peroxide. The method is especially useful as a means for recovering metal surface contaminants on semiconductor grade silicon for analysis of surface contamination of the silicon by such metals. The method is useful for recovering copper from the surface of semiconductor grade silicon in an aqueous solution which can be analyzed directly to determine the amount of copper contamination of the surface of the silicon.

Brief Summary Text - BSTX (11):

The present invention is a method for removing metal contaminants from the surface of silicon metalloid. The method comprises

Brief Summary Text - BSTX (13):

(B) in a second step contacting the silicon metalloid having the metal surface contaminant with an aqueous solution comprising at

least one-half  
weight percent hydrogen peroxide.

Brief Summary Text - BSTX (14):

The silicon metalloid (herein referred to as "silicon") from which metal surface contaminants can be remove by the present method is not limiting and can generally be any composition comprising at least 95 percent by weight of elemental silicon. A preferred silicon for use in the present invention is semiconductor grade silicon. By "semiconductor grade" silicon, it is meant a material comprising at least 99 percent by weight silicon. The physical shape of the silicon is not critical to the present invention and can be in the form of rods, wafers, chunks, and particles. The present method is especially useful for removing metal surface contaminants from silicon chunks intended for use in a process such as the Czochralski method for forming monocrystalline silicon from a melt.

Brief Summary Text - BSTX (17):

In a second step of the present method the silicon having the metal surface contaminant is contacted with an aqueous solution comprising at least one-half weight percent hydrogen peroxide. The weight percent hydrogen peroxide as used herein means the weight percent of hydrogen peroxide in the final weight of water with which the silicon is contacted. Therefore, if an aqueous solution of hydrogen fluoride is used in the first step the volume of water added during this first step would be considered as part of the total water present in the method. It is not necessary that the residual aqueous solution of hydrogen fluoride be present during conduct of the second step. However, a portion of the metal surface contaminants present on the silicon may

be removed during this step and should be accounted for in any subsequent analysis.

Brief Summary Text - BSTX (18):

In the present method it is preferred that the aqueous solution comprise about one to 10 weight percent hydrogen peroxide. Even more preferred is when the aqueous solution comprises about 1.5 to five weight percent hydrogen peroxide. Higher concentrations of hydrogen peroxide may be used if desired.

Brief Summary Text - BSTX (19):

A sufficient volume of the aqueous solution comprising at least one-half weight percent hydrogen peroxide should be added in the second step to ensure a complete wetting of the surface of the silicon. Generally, it is preferred that at least 5 ml of the aqueous hydrogen peroxide solution be present in the method per each 100 g of silicon. Even more preferred is when at least 10 ml of the aqueous hydrogen peroxide solution is present in the method per each 100 g of silicon. The upper limit for the amount of aqueous hydrogen peroxide solution that may be added to the present method is defined by the practicality of handling the volume of the resulting aqueous phase, and by dilution considerations if the aqueous phase is to be analyzed for metals. In a preferred method, about 10 ml to 20 ml of aqueous hydrogen peroxide solution is used per each 100 g of silicon.

Brief Summary Text - BSTX (20):

The temperature at which the silicon is contacted with the aqueous hydrogen peroxide solution is not critical and can generally be within a range of about 15.degree. C. up to the decomposition temperature of the

hydrogen peroxide.

Preferred is when the silicon is contacted with the aqueous solution of

hydrogen peroxide at a temperature within a range of about 20.degree. C. to

30.degree. C. The length of time the silicon is contacted with the aqueous

solution of hydrogen peroxide is not critical and can generally be that

required to ensure a thorough contact with the surface of the silicon.

Generally a contact time of at least one minute is preferred. Even more

preferred is when the silicon is contacted with the aqueous solution of

hydrogen peroxide for about one to ten minutes.

Brief Summary Text - BSTX (21):

The present method is especially useful for removing metal surface

contaminants from silicon for determining the amount of such metals on the

surface of the silicon. By the term "metal surface contaminants" it is meant

any metal or metal compound present on the surface of the silicon. The present

method is useful for removing all metals typically found on the surface of

semiconductor grade silicon, including transition metals and heavy metals.

Metals which may be removed from the silicon include copper, gold, iron,

cobalt, nickel, chromium, tantalum, zinc, tungsten, titanium, magnesium,

molybdenum, and aluminum. The present method is particularly effective in

removing those metals from the surface of silicon where the metal is directly

bonded to silicon atoms. Copper is an example of a metal which may be bonded

directly to silicon atoms and which can be removed from the surface of silicon

by the present method.

Detailed Description Text - DETX (3):

The ability to recover metal contaminants from the

surface of semiconductor grade silicon in aqueous solutions consisting essentially of various concentrations of hydrogen peroxide was evaluated. The semiconductor grade silicon was obtained from a standard commercial process for preparing such silicon by chemical vapor deposition. The silicon was broken into pieces of a size such that three to four pieces weighed about 100 grams. Samples of approximately 100 grams of the silicon were placed in 250 ml acid cleaned Teflon.RTM. containers for testing. Each silicon sample was acid cleaned by standard wet methods to remove surface contamination. Ten microliters of a standard solution containing 12 ppbw Al (ppbw=parts per billion weight), 6 ppbw Fe, 9 ppbw Zn, 6 ppbw Cu, and 9 ppbw Na were added to each sample.

Detailed Description Text - DETX (4):

About 1.5 ml of a 50 weight percent aqueous hydrogen fluoride solution was added to each silicon sample and the Teflon.RTM. container was sealed and allowed to set about 18 hours. At the end of the 18 hours, 8.3 ml of a deionized water solution consisting essentially of hydrogen peroxide at a concentration sufficient to provide a final concentration as described in Table 1 was added to the appropriate silicon samples. The hydrogen peroxide was a commercially obtained unstabilized aqueous hydrogen peroxide solution comprising about 31 to 35 weight percent of hydrogen peroxide, diluted in deionized water as required. The final concentration of hydrogen peroxide is based on the total amount of liquid added to the Teflon.RTM. container. Approximately 0.2 ml of concentrated nitric acid was added to the aqueous solution associated with each silicon sample to reduce the potential for

evaporation of remov d metals during analysis of the solution by graphite furnace atomic adsorption. Each Teflon.RTM. container was shaken sufficiently to insure an adequate rinse of the silicon sample.

Claims Text - CLTX (1):

1. A method for removing metal surface contaminants from a silicon metalloid, the method comprising:

Claims Text - CLTX (3):

(B) in a second step contacting the silicon metalloid having the metal surface contaminant with an aqueous solution consisting essentially of at least one-half weight percent hydrogen peroxide.

Claims Text - CLTX (9):

7. A method according to claim 1, where the aqueous solution of the second step comprises about one to 10 weight percent hydrogen peroxide.

Claims Text - CLTX (10):

8. A method according to claim 1, where the aqueous solution of the second step comprises about 1.5 to five weight percent hydrogen peroxide.

Claims Text - CLTX (11):

9. A method according to claim 1, where the contacting of the second step is effected at a temperature within a range of about 15.degree. C. up to the decomposition temperature of the hydrogen peroxide.

Claims Text - CLTX (16):

(B) in a second step contacting the semiconductor grade silicon metalloid with an aqueous solution consisting essentially of at least one-half weight



percent hydrogen peroxide thereby forming an aqueous phase containing the metal surface contaminant, and

Claims Text - CLTX (19):

14. A method according to claim 12, where the aqueous solution of the second step comprises about one to 10 weight percent hydrogen peroxide.

Claims Text - CLTX (20):

15. A method according to claim 12, where the aqueous solution of the second step comprises about 1.5 to five weight percent hydrogen peroxide.

Claims Text - CLTX (27):

(B) in a second step contacting the semiconductor grade silicon metalloid with about 10 ml to 20 ml per 100 g of silicon of an aqueous solution consisting essentially of about 1.5 to five weight percent hydrogen peroxide thereby forming an aqueous phase containing the copper, and

L Number	Hits	Search Text	DB	Time stamp
2	354	etchant with spray	USPAT; US-PGPUB	2003/07/08 13:02
3	26	(etchant with spray) and (etchant with (hydrogen adj peroxide))	USPAT; US-PGPUB	2003/07/08 13:02

US-PAT-NO: 4462861

DOCUMENT-IDENTIFIER: US 4462861 A

TITLE: Etchant with increased etch rate

----- KWIC -----

Brief Summary Text - BSTX (3):

This invention relates to an etchant comprising sulfuric acid activated with hydrogen peroxide and characterized by an enhanced etch rate. The etchant is particularly useful in the manufacture of printing circuit boards.

Brief Summary Text - BSTX (6):

Activation of dilute sulfuric acid with hydrogen peroxide is most attractive due to low cost and ease of electrolytic copper recovery from the spent etchant prior to disposal. However, the utility of hydrogen peroxide etching solutions is reduced somewhat due to catalyzed decomposition of hydrogen peroxide caused by etched metal ions or other transition metal ions in solution and a slow etch rate, typically 1.4 mils of copper from 1 ounce copper clad laminate in 10-25 minutes at 120.degree. F. To enhance or exalt etch rate, more concentrated solutions of hydrogen peroxide have been used, but concentrated peroxide solutions are hazardous to health and safety. In addition, such etchants have not been successfully used with tin dissimilar metal etch resists because they attack tin, especially immersion tin.

Brief Summary Text - BSTX (7):

In U.S. Pat. No. 4,130,454, incorporated herein by

reference, a modified peroxide etch is disclosed and claimed. The etchant comprises hydrogen peroxide and a molybdenum compound in an acidic solution. The hydrogen peroxide provides a sustained etch rate and the molybdenum etches at a substantially greater rate than the peroxide thereby exalting the rate to a desired level for commercial use. Molybdenum cannot be used as a sole oxidant because it is rapidly depleted due to reduction to a lower valence form as etching proceeds. It is therefore incapable of providing sustained etching. Patentee proposes a theory that the combination of peroxide and molybdenum is a synergistic combination because both are believed to etch the peroxide in the acid environment while providing the secondary function of oxidizing molybdenum to a higher valence capable of etching metals in the acidified environment.

Brief Summary Text - BSTX (8):

The peroxide etchants described above are used to etch copper both by immersion and by spraying. Immersion etching comprises immersing a part within the etchant until the desired amount of metal is dissolved.

Spray etching comprises spraying a finely divided stream of etchant against the surface of the part until the desired amount of metal is dissolved.

Spray etching generally provides the advantage of a more rapid etch rate because the finely divided droplets of etchant are aerated resulting in additional oxygen at the surface of the part being etched and a concomitant increase in etch rate.

Brief Summary Text - BSTX (9):

The etchants of the aforesaid U.S. Pat. No. 4,130,454 do provide the exalted etch rate as reported in the patent for immersion

etching. However,  
for spray etching, the etch rate appears to be retarded  
rather than exalted  
which is contrary to that which would be expected.  
Consequently, the etchant  
of said patent is usable for spray etching, but spray  
etching of said etchant  
may not be commercially practical where high through put of  
parts is required.

Brief Summary Text - BSTX (11):

The invention described herein is a peroxide etchant  
especially useful for  
rapidly dissolving large quantities of copper containing  
metals--i.e., copper  
and its alloys. The etchant is characterized by an exalted  
etch rate when used  
in both the immersion and spray modes. For immersion  
etching, the etchant of  
the invention has an etch rate comparable to the etchants  
of the aforesaid  
patent utilizing molybdenum as the exaltant and are able to  
dissolve all of the  
copper from a one ounce copper clad circuit board base  
material in from about 6  
to 8 minutes, dependent upon the specific formulation used.

For spray etching,  
the etchants are capable of dissolving all of the copper  
from one ounce copper  
clad base material in about 1.5 to 3 minutes compared to  
from about 10 to 15  
minutes for those etchants using molybdenum as the  
exaltant.

Detailed Description Text - DETX (6):

The procedure of examples 10 and 11 was repeated  
substituting acetic acid  
for propionic acid. The acetic used was a 98% solution and  
added in an amount  
of 40 ml per liter. With a fresh etchant, the spray time  
was 20 minutes.  
After 20 minutes of use, the spray time was 5.5 minutes  
indicating that an  
aging process of some sort might be necessary for acetic  
acid.

Claims Text - CLTX (23):

23. A process for exalting the etch rate of a hydrogen peroxide-sulfuric acid etchant, said process comprising adding a low molecular weight carboxylic acid to the etchant in a concentration sufficient to double the etch rate compared to an etchant free of the carboxylic acid.

L Number	Hits	Search Text	DB	Time stamp
2	354	etchant with spray	USPAT; US-PGPUB	2003/07/08 13:02
3	26	(etchant with spray) and (etchant with (hydrogen adj peroxide))	USPAT; US-PGPUB	2003/07/08 13:21
5	0	((etchant with spray) and (etchant with (hydrogen adj peroxide)) and (etch\$3 with molybdenum)) not ((etchant with spray) and (etchant with (hydrogen adj peroxide)))	USPAT; US-PGPUB	2003/07/08 13:22
4	2	(etchant with spray) and (etchant with (hydrogen adj peroxide)) and (etch\$3 with molybdenum)	USPAT; US-PGPUB	2003/07/08 13:27
6	1	("4130454").PN.	USPAT; US-PGPUB	2003/07/08 13:24
7	28	(etchant with (hydrogen adj peroxide)) and (etch\$3 with molybdenum)	USPAT; US-PGPUB	2003/07/08 14:22
8	3	(etchant with (hydrogen adj peroxide)) and (etch\$3 with molybdenum)	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 14:22
9	1	("4747907").PN.	USPAT; US-PGPUB	2003/07/08 14:13
10	9	(etch\$3 with molybdenum) and (surfactant or inhibit\$3)	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 15:19
11	193	(etch\$3 with molybdenum) and (surfactant or inhibit\$3)	USPAT; US-PGPUB	2003/07/08 14:26
12	20	((etch\$3 with molybdenum) and (surfactant or inhibit\$3)) and (corrosion with inhibit\$3)	USPAT; US-PGPUB	2003/07/08 14:32
13	12	((etch\$3 with molybdenum) and (surfactant or inhibit\$3)) and citrate	USPAT; US-PGPUB	2003/07/08 14:32
14	165	etchant same (surfactant or inhibit\$3)	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 15:20
15	80	etchant same (surfactant or (corrosion with inhibit\$3))	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 15:22
16	3	(etchant same (surfactant or (corrosion with inhibit\$3))) and (hydrogen adj peroxide)	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 15:23
17	351	etchant same (surfactant or (corrosion with inhibit\$3))	USPAT; US-PGPUB	2003/07/08 15:39
18	122	(etchant same (surfactant or (corrosion with inhibit\$3))) and (hydrogen adj peroxide)	USPAT; US-PGPUB	2003/07/08 15:39
19	79	((etchant same (surfactant or (corrosion with inhibit\$3))) and (hydrogen adj peroxide)) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 15:39
20	6	((etchant same (surfactant or (corrosion with inhibit\$3))) and (hydrogen adj peroxide)) and @ad<=20000320 and molybdenum	USPAT; US-PGPUB	2003/07/08 15:47
22	64	(wet with etching) same (surfactant or (corrosion with inhibit\$3))	USPAT; US-PGPUB	2003/07/08 15:39
23	45	((wet with etching) same (surfactant or (corrosion with inhibit\$3))) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 16:04
24	13	((wet with etching) same (surfactant or (corrosion with inhibit\$3))) and @ad<=20000320 and (hydrogen adj peroxide)	USPAT; US-PGPUB	2003/07/08 15:46
25	2365	(hydrogen adj peroxide) same (surfactant)	USPAT; US-PGPUB	2003/07/08 16:23
26	265	((hydrogen adj peroxide) same (surfactant)) and etching	USPAT; US-PGPUB	2003/07/08 15:47
27	174	((hydrogen adj peroxide) same (surfactant)) and etching) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 15:47

28	11	((((hydrogen adj peroxide) same (surfactant)) and etching) and @ad<=20000320) and molybdenum	USPAT; US-PGPUB	2003/07/08 15:47
29	38	(etching or etchant) same ((sodium adj dihydrogen adj citrate) or (disodium adj hydrogen) or (trisodium adj citrate) or (ammonium adj acetate))	USPAT; US-PGPUB	2003/07/08 16:18
30	26	((etching or etchant) same ((sodium adj dihydrogen adj citrate) or (disodium adj hydrogen) or (trisodium adj citrate) or (ammonium adj acetate))) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 16:19
31	407	(etching or etchant) same (water with resistance)	USPAT; US-PGPUB	2003/07/08 16:23
32	32	((etching or etchant) same (water with resistance) ) and (hydrogen adj peroxide)	USPAT; US-PGPUB	2003/07/08 16:19
33	19	((etching or etchant) same (water with resistance) ) and (hydrogen adj peroxide) ) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 16:23
34	30506	(water near3 resistance)	USPAT; US-PGPUB	2003/07/08 16:47
35	1730	((water near3 resistance) ) and (etching or etchant)	USPAT; US-PGPUB	2003/07/08 16:23
36	157	((water near3 resistance) ) and (etching or etchant) ) and (hydrogen adj peroxide)	USPAT; US-PGPUB	2003/07/08 16:23
37	117	((water near3 resistance) ) and (etching or etchant) ) and (hydrogen adj peroxide) ) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 16:40
38	117	((water near3 resistance) ) and (etching or etchant) ) and (hydrogen adj peroxide) ) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 16:52
39	12	etchant same (water near3 resistance)	USPAT; US-PGPUB	2003/07/08 16:52
40	3	etchant same (water near3 resistance)	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 16:49
41	199	etching same (water near3 resistance)	USPAT; US-PGPUB	2003/07/08 17:02
42	138	(etching same (water near3 resistance) ) and @ad<=20000320	USPAT; US-PGPUB	2003/07/08 16:53
43	97	etching same (water near3 resistance)	EPO; JPO; DERWENT; IBM_TDB	2003/07/08 17:02



US-PAT-NO: 6242331

DOCUMENT-IDENTIFIER: US 6242331 B1

TITLE: Method to reduce device contact  
resistance using a hydrogen peroxide treatment

----- KWIC -----

Claims Text - CLTX (9):

6. The method of claim 1 where the resistance of said deionized water is between 16 and 22 megohm-cm.

Claims Text - CLTX (27):

14. The method of claim 7 where the resistance of said deionized water is between 16 and 22 megohm-cm.

Claims Text - CLTX (47):

23. The method of claim 15 where the resistance of said deionized water is between 16 and 22 megohm-cm.

Claims Text - CLTX (66):

32. The method of claim 24 where the resistance of said deionized water is between 16 and 22 megohm-cm.

US-PAT-NO: 5698503

DOCUMENT-IDENTIFIER: US 5698503 A

TITLE: Stripping and cleaning composition

----- KWIC -----

Application Filing Date - AD (1):

19961108

Detailed Description Text - DETX (7):

Other additives normally used in buffered oxide etchant solutions may be included in the novel etching solutions of the present invention. For example, polar solvent diluents such as acetic acid and ammonium acetate may be included. Ammonium acid phosphate buffers represent another choice.

TDB-ACC-NO: NN69031246

DISCLOSURE TITLE: Etching of Molybdenum Thin Films. March 1969.

PUBLICATION-DATA: IBM Technical Disclosure Bulletin, March 1969, US

VOLUME NUMBER: 11

ISSUE NUMBER: 10

PAGE NUMBER: 1246

PUBLICATION-DATE: March 1, 1969 (19690301)

CROSS REFERENCE: 0018-8689-11-10-1246

DISCLOSURE TEXT:

1p. Molybdenum films can be etched in a manner which produces

a sloping edge to the land pattern when using a photoresist mask.

The etchant consists of 25 parts of 30% hydrogen peroxide 120 parts

of 90% formic acid and 10 parts water. At 35 degrees centigrade, an

etch rate of about 3000 Angstroms per minute can be realized.

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DERWENT-ACC-NO: 1970-57654R

DERWENT-WEEK: 197032

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TITLE: Chemical etching of molybdenum in  
nit - ric acid

PATENT-ASSIGNEE: MOSCOW FOOD INDUSTRY INST[FOOD]

PRIORITY-DATA: 1967SU-1183930 (September 12, 1967)

PATENT-FAMILY:

PUB-NO	PAGES	PUB-DATE	MAIN-IPC
LANGUAGE			
SU 254998 A			N/A
000	N/A		

INT-CL (IPC): C23F000/00

ABSTRACTED-PUB-NO: SU 254998A

BASIC-ABSTRACT:

CHEMICAL ETCHING OF MOLYBDENUM IN NITRIC ACID SOLN. is characterized in that hydrazine derivatives, for ex. hydrazine, hydrazine chloride and phenylhydrazine, hydroxylamine, urea, thiourea are used as inhibitors in the amount from 1 to 50 mili-moles per litre of the nitric acid solu. The process is carried out at 20-80 degrees C. Use of the proposed inhibitors slows down dissolution of molybdenum, permits control of the process, and by carrying the etching period permits removal of the surface layers of the desired thickness, i.e. prevents over-etching and thus reduces losses of the expensive metal and consumption of the acid. The amount of gas evolved during the etching is considerably reduced thus improving working conditions.

The proposed concns.  
of the inhibitors prevent formation of acid insoluble films  
on the surfaces of  
the molybdenum being etched and these inhibitors are easily  
removed from the  
metal by washing with water.

TITLE-TERMS: CHEMICAL ETCH MOLYBDENUM ACID

DERWENT-CLASS: M14

CPI-CODES: M14-A;

US-PAT-NO: 5798426

DOCUMENT-IDENTIFIER: US 5798426 A

TITLE: Acrylic polymer compounds

----- KWIC -----

Detailed Description Paragraph Table - DETL (2):

TABLE II		Test	
Data	Water Oil		
Appearance	Resistance	Resistance	(Note 1) (Note 2)
(Note 3)			
		Example 11	Clear
Glossy	-- -- AMP salt		
of Example 1	Film	Example 12	Clear Glossy
of Example 1	Film		-- -- TEA salt
Example 13	Clear Glossy	Fair Fair	Ammonium salt of
Example 1	Film	Example	
14	Clear Glossy	Poor --	Emulsion of Example 1
Example 15	Clear Glossy		
Good Fair	Ammonium salt of Example 8	Film	Example 16
Clear Glossy	Excellent		
Fair	Ammonium salt of Example 9	Film	

Note 1: Appearance refers to gloss, clarity, and integrity of the dry film formed. Note 2: Water Resistance refers to the degree of etching/deformation of the film as a result of contact with a drop of water for 5 minutes. Ratings are excellent, good, fair and poor. Note 3: Oil resistance refers to the degree of etching/deformation of the film as a result of contact with a drop of commercial hand cream lotion ( mixture of water, cetyl esters, petroleum, isopropyl palmitate, triethanolamine, steryl alcohol, lanolin, methylparaben, propylparaben and other) for 5 minutes. Rating are excellent, good, fair and poor. Note 4: Adhesion refers to the difficulty of removing the

dried film from the glass plate when subjected to water temperatures of room temperature up to 70.degree. C. The higher the temperature and/or the longer the time required to soak off the film, the stronger the adhesion of the film to the glass plate. An adhesion scale of 1-10 was used, with 1 being the best adhesion and 10 being the worst in adhesion and easiest to soak off the glass plate.



DERWENT-ACC-NO: 2002-222841

DERWENT-WEEK: 200228

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TITLE: Etchant for etching tri-layered  
metallic film of  
mo/al-nd/mo

INVENTOR: KIM, G S; KIM, S S ; LEE, Y H ; PARK, M C ; SONG,  
H S

PATENT-ASSIGNEE: DONGWOO FINE CHEM CO LTD[DONGN]

PRIORITY-DATA: 2000KR-0004889 (February 1, 2000)

PATENT-FAMILY:

PUB-NO	PAGES	PUB-DATE	MAIN-IPC
KR 2001077228 A		August 17, 2001	N/A
000		H01L 029/786	

APPLICATION-DATA:

PUB-NO	APPL-DATE	APPL-DESCRIPTOR	APPL-NO
KR2001077228A		N/A	
2000KR-0004889		February 1, 2000	

INT-CL (IPC): H01L029/786

ABSTRACTED-PUB-NO: KR2001077228A

BASIC-ABSTRACT:

NOVELTY - An etchant for etching a tri-layered metallic film of Mo/Al-Nd/Mo is provided, which can etch the tri-layered metallic film of Mo/Al-Nd/Mo without undercut phenomenon of a bottom Mo layer while forming a metal line of a TFT-LCD.

DETAILED DESCRIPTION - A tri-layered metallic film of

Mo/Al-Nd/Mo is used as a source/drain array metal line. And the etchant includes H3PO4 of 68-74 wt%, HNO3 of 2-4 wt%, CH3COOH of 5-15wt% and water. And the etchant also includes an additive of 0.01-0.105 wt% of the whole composition. The etchant also includes H3PO4 of 70-74 wt%, HNO3 of 2-4 wt%, CH3COOH of 8-15wt%, water and an additive of 0.01-0.03 wt%. The water is an ultra pure water having a resistance above 18M ohm.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: ETCH ETCH TRI LAYER METALLIC FILM AL

DERWENT-CLASS: L03 U11

CPI-CODES: L04-C07C1;

EPI-CODES: U11-A10;

SECONDARY-ACC-NO:

CPI Secondary Accession Numbers: C2002-068192



US005698503A

**United States Patent** [19]

Ward et al.

[11] Patent Number: 5,698,503

[45] Date of Patent: Dec. 16, 1997

[54] **STRIPPING AND CLEANING COMPOSITION**

[75] Inventors: Irl E. Ward, Bethlehem; Francis W. Michelotti, Easton, both of Pa.; Darryl W. Peters, Stewartsville, N.J.

[73] Assignee: Ashland Inc., Dublin, Ohio

[21] Appl. No.: 745,754

[22] Filed: Nov. 8, 1996

[51] Int. Cl.<sup>6</sup> ..... C11D 7/08; C11D 7/50; C09K 13/08; B08B 3/08

[52] U.S. Cl. .... 510/176; 510/175; 510/255; 510/257; 510/259; 510/475; 510/421; 510/493; 134/2; 134/40; 134/41; 134/42

[58] Field of Search ..... 510/176, 255, 510/257, 259, 475, 421, 493, 175; 134/2, 40, 41, 42

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Primary Examiner—Douglas J. McGinty  
 Attorney, Agent, or Firm—John Lezdey

[57] **ABSTRACT**

An aqueous and acidic stripping and cleaning composition is provided which contains a polyhydric alcohol, ammonium fluoride, dimethylsulfoxide and water. The pH of the composition is greater than about 4 but less than 7. Also provided is a method of stripping and cleaning utilizing the compositions of the invention. Optionally, the composition may contain a phosphate buffer.

**15 Claims, 3 Drawing Sheets**

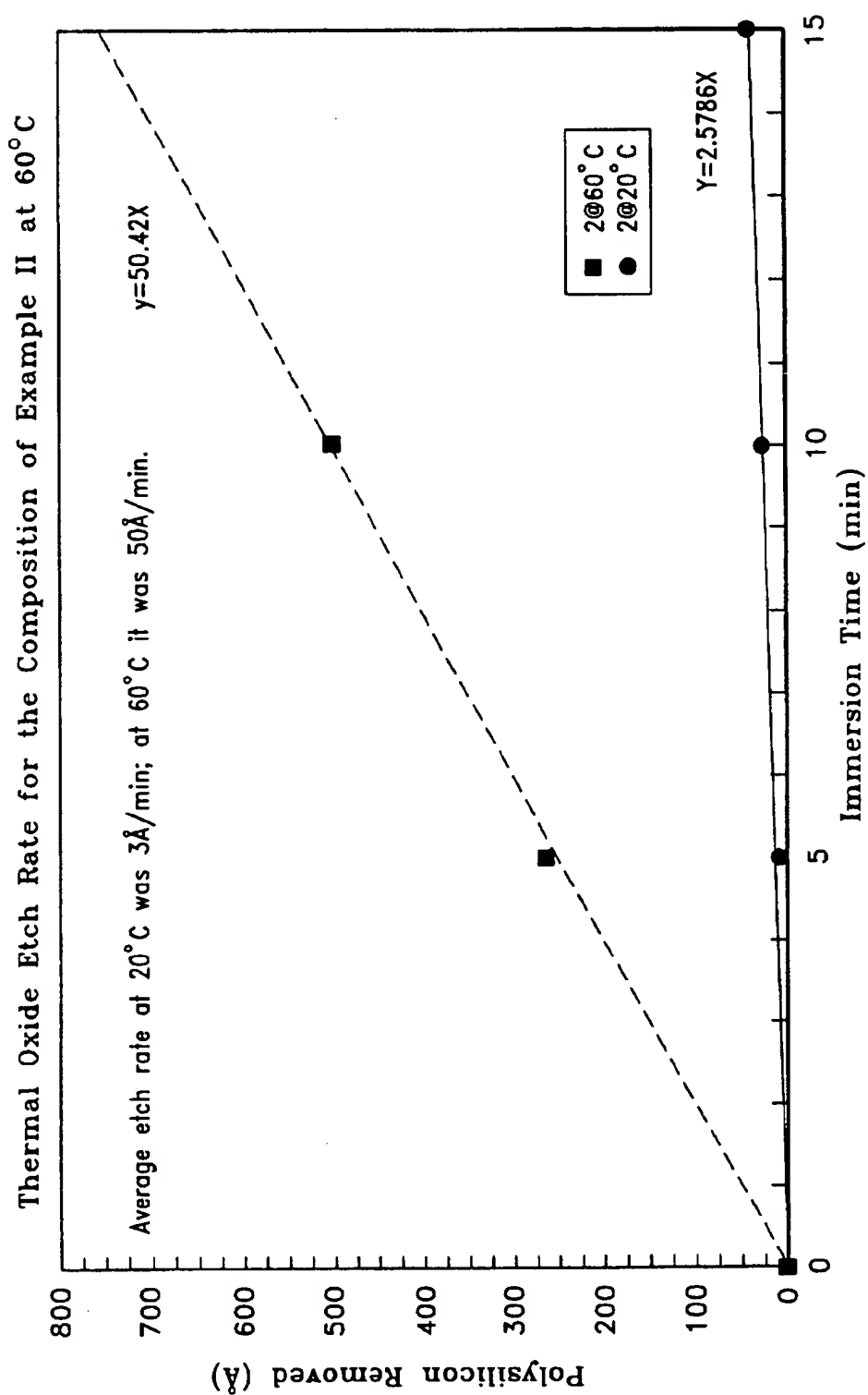
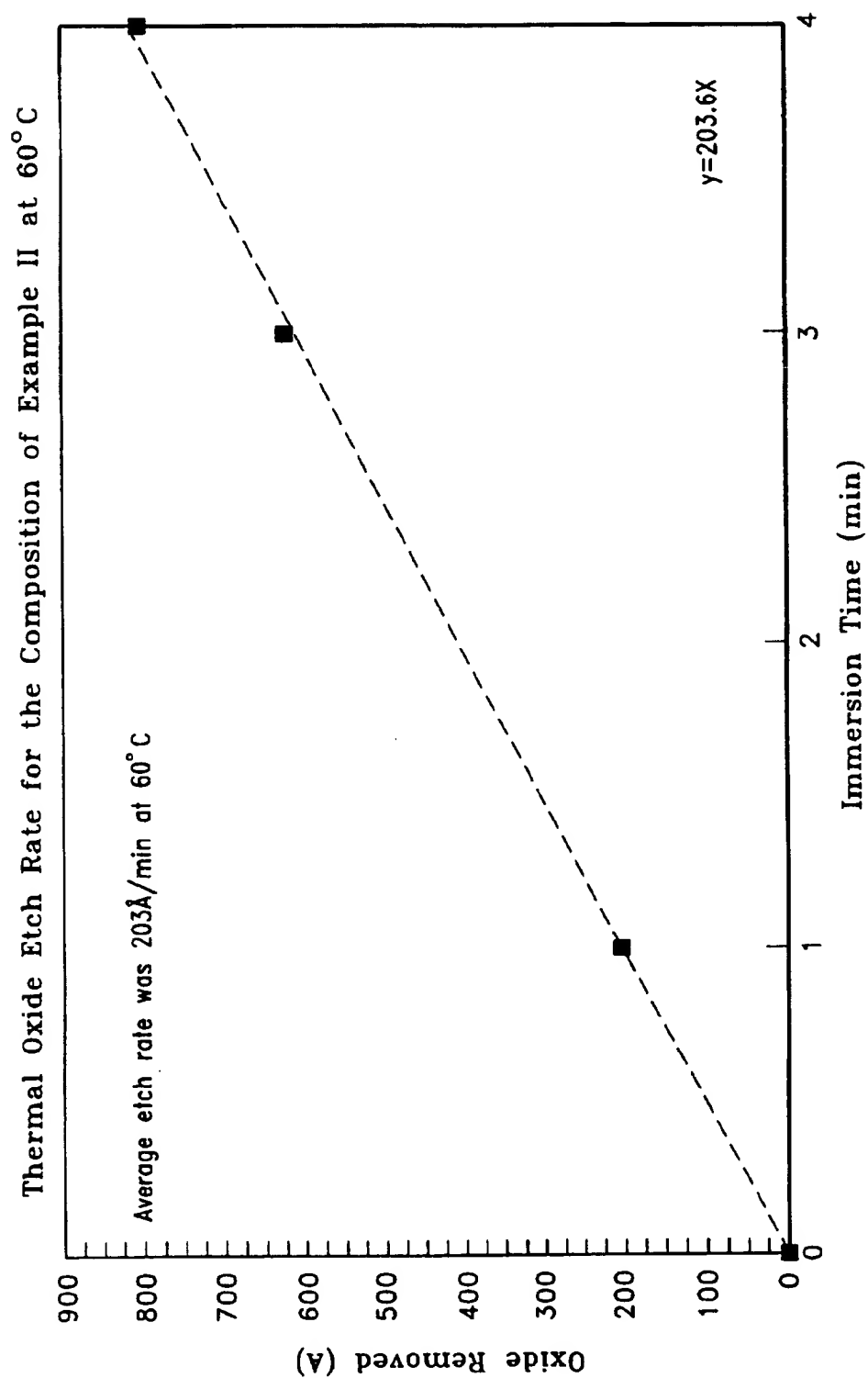
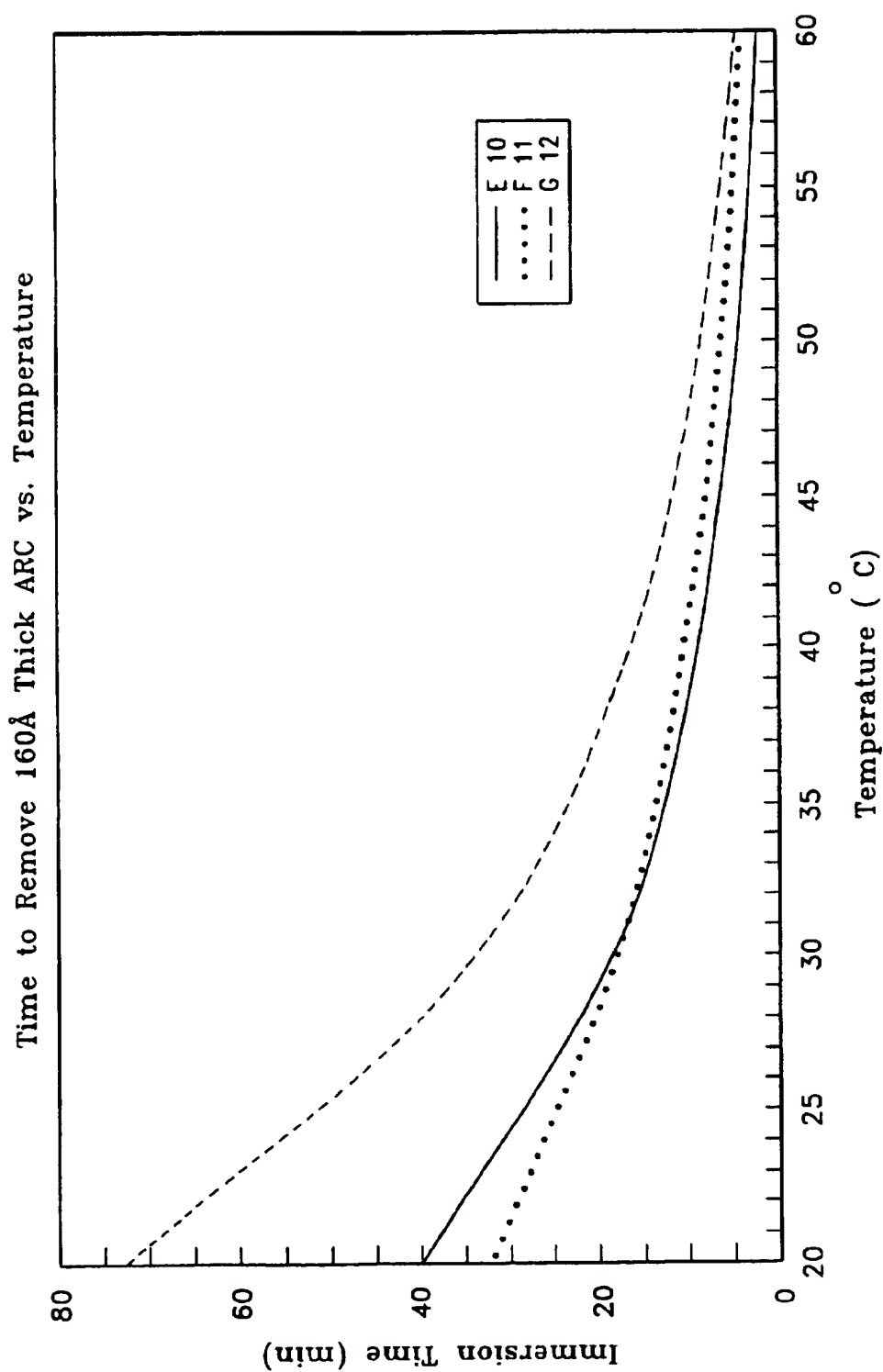


FIG. 1

*FIG. 2*

*FIG. 3*

## STRIPPING AND CLEANING COMPOSITION

## FIELD OF THE INVENTION

The invention relates generally to a stripping and cleaning composition having a controlled oxide etch and sidewall polymer removal capability and to a process for stripping and etching utilizing the composition. More particularly, the invention provides a slightly acidic stripping composition containing ammonium fluoride and a water soluble polar solvent which is free of ethylene glycol and hydrogen fluoride. Optionally, the compositions may contain a phosphate buffer.

## BRIEF DESCRIPTION OF THE PRIOR ART

In fabricating semiconductor devices it is the practice to passivate and protect the surface of a body of silicon material with a layer or superimposed layers of inorganic insulating materials, such as silicon dioxide, silicon nitride, etc.

Openings are made through these protective layers to the silicon body both to provide semiconductive doped regions within the body as well as to allow conductive layers on top of the body to make contact to the semiconductive regions. In most instances it is important that the etchant be selective, i.e., it exhibits the property of selectively attacking the silicon vs. oxide or the other substrate or deposited layer. For example, dilute hydrofluoric acid buffered with ammonium fluoride has been used to etch silicon dioxide because it does not substantially attack silicon nitride or silicon. Similarly, hot phosphoric acid will attack silicon nitride while not attacking silicon dioxide, silicon or common photoresist layers.

However, the standard buffered HF solution will attack P+ or N doped silicon formed during semiconductor processing. This is particularly true when the etching solution is in contact simultaneously with exposed highly doped silicon and platinum silicide. The cause is possibly an electrochemical reaction between the silicon and the platinum silicide, with the reaction connection being completed when the semiconductor is dipped into the standard buffered HF solution. This tends to dissolve the silicon, especially P+ silicon.

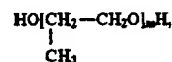
Kinstron et al, U.S. Pat. No. 4,343,677 discusses film patterning and disclose an etching solution which uses buffered ammonium fluoride/hydrofluoric acid in a molar ratio of about ten to one, mixed with a suitable solvent such as ethylene glycol. Gajda, U.S. Pat. No. 4,230,523, discloses an etchant comprised of a solution of hydrogen fluoride dissolved in organic solvents such as glycerine or another polyhydric alcohol. The etchant is used for etching silicon dioxide while not attacking silicon. Gajda requires that the solution be free of unbound water and ammonium fluoride. Maeda et al, U.S. Pat. No. 3,979,241, teach an etching liquid with ammonium fluoride or an alkali fluoride dissolved in a polyhydric alcohol, such as ethylene glycol, polyethylene glycol, and glycerine. The etching solution is used for selectively etching silicon dioxide or silicon nitride on a semiconductor wafer.

U.S. Pat. No. 5,320,709 to Bowden et al discloses a composition for selectively removing oxidized organometallic residues, oxidized organosilicon residues and oxides with a composition which is essentially pH neutral and comprises a polyhydric alcohol and an anhydrous ammonium fluoride salt. The present invention provides a specific improvement over the compositions of this patent by utilizing aqueous ammonium fluoride and an organic polar solvent in a buffered acidic pH.

## SUMMARY OF THE INVENTION

The present invention provides an aqueous acidic stripping and cleaning composition for the removal of organic materials, organometallic residues, organosilicon residues, sidewall polymer (SWP) and inorganic residues which has a controlled oxide etch rate. The buffered acidic composition which has a pH of more than 4 and less than 7 comprises the admixture of:

- a) about 55 to 85% by weight of a polyhydric alcohol having the formula selected from the group consisting of  $\text{HO}[\text{CH}_2-\text{CH}_2\text{O}]_n\text{H}$  and



more;

- b) about 5 to 35% by weight of an organic water soluble polar solvent;

- c) about 0.5 to 20% by weight of ammonium fluoride; and
- d) the remainder being water typically in the range of about 1-20%.

Generally, the ammonium fluoride is used as a 40% aqueous solution.

The preferred polar solvents used in the invention are dimethylsulfoxide, dimethyl acetamide (DMAC), N-methylpyrrolidone, gamma butyrolactone, and the like.

The compositions of the inventions are suitable for both VIA and contact hole applications as well as connector lead/multi-layer metal stack applications due to their high resistance to metal and metal alloy corrosion.

Advantageously, the compositions of the invention are free of ethylene glycol and hydrofluoric acid.

The compositions of the invention may contain a corrosion inhibitor.

It is a general object of the invention to provide a cleaning and stripping composition having a controlled etch and sidewall polymer removal capability.

It is another object of the invention to provide a stripping composition which is free of ethylene glycol and hydrofluoric acid.

It is yet another object of the invention to provide a stripping composition which is water soluble having high resistance to metal corrosion.

It is still another objection of the invention to provide a cleaning composition which removes inorganic and ash residues.

It is still another objection of the invention to provide a method for stripping which provides for a silicon or controlled oxide etch.

The advantages and further objects of the invention will become more apparent from the following description of the preferred embodiments and the drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates the undoped polysilicon etch rate of the compositions of the invention.

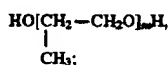
FIG. 2 illustrates the thermal oxide etch rate of the compositions of the invention.

FIG. 3 illustrates the time to remove 160Å thick ARC vs. temperature with the compositions of the invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to a slightly acidic stripping and cleaning composition comprising a polyhydric

alcohol having the formula selected from the group consisting of  $\text{HO}[\text{CH}_2-\text{CH}_2\text{O}]_n\text{H}$  and



more, dimethylsulfoxide or the like, ammonium fluoride and a medium having a pH of more than about 4 but less than 7. Advantageously, the composition contains a corrosion inhibitor which forms a 5- or 6- membered ring coordination complex with a metal substrate as described in copending application Ser. No. 07/983,257 or an alkylated phenol.

The compositions of the present invention are particularly suitable for removing organic or inorganic material from a substrate such as sidewall polymers (SWP) and/or for controlled etching of contaminated or uncontaminated oxide surfaces. The composition are also effective in removing many forms of resist ash and etch residues without the presence of hydrogen fluoride.

The stripping and cleaning compositions of the invention contain about 65 to 85% by weight of composition of a polyhydric alcohol which excludes ethylene glycol, for example propylene glycol, glycerol, polyethylene glycol, etc.

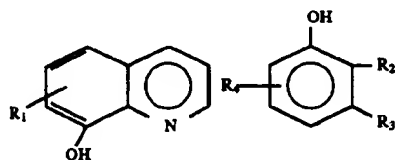
Ammonium fluoride in an amount of about 0.5 to 20% by weight of composition is an essential component of the composition. Ammonium fluoride is commercially available as a 40% aqueous solution.

The use of about 5 to 35% by weight of dimethylsulfoxide, together with a polyhydric alcohol other than ethylene glycol, surprisingly stabilizes the performance of the formulations and enhances their process latitude at elevated temperatures. The use of water with DMSO and the like as the solvent allows use of ammonium fluoride in the formulation when propylene glycol is the polyhydric alcohol.

Other additives normally used in buffered oxide etchant solutions may be included in the novel etching solutions of the present invention. For example, polar solvent diluents such as acetic acid and ammonium acetate may be included. Ammonium acid phosphate buffers represent another choice.

These additives may be used in an amount of up to about 20% by weight, for example.

Corrosion inhibitors in an amount of up to about 15% by weight can be added to the stripping compositions. Preferably, the inhibitor concentration is from about 0.5 to 8% by weight, and most preferably, about 5% by weight. Suitable inhibitors are disclosed in U.S. Pat. No. 5,417,877 to Ward et al. which is herein incorporated by reference. The inhibitor is a compound selected from the group consisting of:



wherein  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are the same or different and each represent lower alkyl, H, OH,  $\text{NHR}_5$ ,  $\text{CO}_2\text{R}_6$ ,  $\text{COR}_7$  and SH, wherein  $R_5$  and  $R_6$  are the same or different and each represent H or lower alkyl, and  $R_7$  represents lower alkyl, with the proviso that when  $R_4$  is H, not more than one of  $R_1$ ,  $R_2$  and  $R_3$  is the same as  $R_4$ , and when  $R_3$  is not H, not more

than one of  $R_1$ ,  $R_2$  and  $R_4$  is hydrogen, the remainder being the same or different than  $R_3$ . Preferred inhibitors include catechol, pyrogallol, anthranilic acid, gallic acid, gallic esters, and the like.

The compositions of this invention are especially useful and advantageous for numerous reasons among which may be mentioned the following. The compositions are water soluble, non-corrosive to substrate, non-flammable and of low toxicity to the environment. The compositions evidence high stripping and cleaning efficiency at low temperatures for a wide variety of coating residues and substrates. The compositions are particularly suitable for removal of residues from plasma processing used in integrated circuit fabrication since they also prevent the redeposition of metal ions, especially sodium and potassium ions and have a faster more complete removal of trace metals. The compositions provide controlled oxide etch and controlled silicon and/or polysilicon and/or silicon nitride etch.

The process of the invention is carried out by contacting a substrate containing an organic or metal-organic polymer, inorganic salt, oxide, hydroxide or complex or combination thereof as a film or residue, (e.g. sidewall polymer (SWP)), with the described stripping composition. The actual conditions, e.g., temperature, time, etc., depend on the nature and thickness of the complex (photoresist and/or SWP) material to be removed, as well as other factors familiar to those skilled in the art. In general, for stripping, the substrate is contacted or dipped into a vessel containing the stripping composition at an elevated temperature, preferably between  $25^\circ\text{--}80^\circ\text{C}$ . and usually about  $25^\circ\text{--}40^\circ\text{C}$ . for a period of about 1–15 minutes and then rinsed with water.

Representative organic polymeric materials include positive photoresists, electron beam resists, X-ray resists, ion beam resists, and the like. Specific examples of organic polymeric materials include positive resists containing phenolformaldehyde resins or poly (p-vinylphenol), polymethylmethacrylate-containing resists, and the like. Examples of plasma processing residues side wall polymers (SWP) include among others, metal-organic complexes and/or inorganic salts, oxides, hydroxides or complexes which form films or residues either alone or in combination with the organic polymer resins of a photoresist. The organic materials and/or SWP can be removed from conventional substrates known to those skilled in the art, such as silicon, silicon dioxide, aluminum, aluminum alloys, copper, copper alloys, etc.

Examples illustrating the removal of a coating from a substrate under varying conditions are described further below. The following examples are provided to further illustrate the invention and are not intended to limit the scope of the present invention.

Examples of compositions according to the invention are set forth below in Table I. The amounts indicated are in percent by weight of composition.

TABLE I

Stripping Compositions	Propylene Glycol (wt %)	DMSO (wt %)	40% aq. Ammonium Fluoride
A	77.5	20.0	2.5
B	76.3	18.7	5.0
C	73.2	16.8	10.0
D	68.7	11.3	20.0

The undoped polysilicon etch rate for composition B at  $20^\circ\text{C}$ . and  $60^\circ\text{C}$ . is shown in FIG. 1. The average etch rate at  $20^\circ\text{C}$ . was  $3\text{\AA}/\text{min}$  and at  $60^\circ\text{C}$ .  $50\text{\AA}/\text{min}$ .



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## EXAMPLE I

A stripping and cleaning composition was prepared by admixing the following ingredients:

Ingredient	% Wt.
Propylene glycol	77.5
DMSO	16.3
40% ammonium fluoride	5.0
Acetic acid	0.5
Ammonium acetate	0.7

The pH of the composition is 5.2.

## EXAMPLE II

A stripping and cleaning composition was prepared by admixing the following ingredients:

Ingredient	% Wt.
Propylene glycol	73.0
DMSO	12.3
Ammonium fluoride	5.0
Acetic acid	4.0
Ammonium acetate	5.2
Catechol	0.5

The pH of the composition is 4.8.

The thermal oxide etch rate for the composition of Example II at 60° C. is shown in FIG. 2. The average etch rate at 60° C. was 203 Å/min.

## EXAMPLE III

A stripping and cleaning composition was prepared by admixing the following ingredients:

Ingredient	% Wt.
Propylene glycol	73.0
DMSO	12.0
Ammonium fluoride	5.0
Catechol	0.5
Buffer*	9.5
	100%

The buffer solution was prepared from a range of 7% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and 3% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> to 9% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and 3% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> to 9% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and 1% (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, the remainder being deionized water.

## EXAMPLE IV

Example III illustrates the removal of a photoresist from a substrate using a stripping composition of the invention.

More specifically, an immersion tank containing composition A of Table I is held at room temperature and the stripping composition is recirculated at an exchange rate of about 1.0 (i.e. pump flow rate/bath volume~1.0).

A rinse tank with standard overflow cascade containing deionized water with a CO<sub>2</sub> sparge is also prepared.

The photoresist wafer specimen is immersed into the stripping composition for 1-20 minutes in accordance with the oxide etch rate and the amount of removal desired.

The specimen is removed from the stripping bath and immersed into the rinse tank for 2-4 minutes using continuous CO<sub>2</sub> sparging.

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The specimen is then removed and spun dry in a heated nitrogen atmosphere.

## EXAMPLE V

Table II shows the admixture of components together with buffering additives.

The time to remove 160 Å thick ARC vs. temperature of compositions E, F and G is shown in FIG. 3.

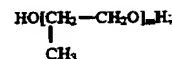
TABLE II

COMPONENT	E	F	G
Propylene glycol	68.4	75.9	64.2
DMSO	12.4	12.4	12.4
NH <sub>4</sub> F (40%)	10.0	2.5	5.0
HOAc (glacial)	4.0	4.0	8.0
NH <sub>4</sub> OAc (salt)	5.2	5.2	10.4
pH (5% aqueous sol'n)	4.8	4.8	4.8
ER <sub>TOX</sub> @ RT (Å/min)	12.4	3	4.6
ER <sub>TOX</sub> @ 60° C. (Å/min)	348	78	141
ER <sub>PE</sub> @ RT (Å/min)	4	5	2.2
ER <sub>PE</sub> 60° C. (Å/min)	71	44	37

What is claimed is:

1. An aqueous and acidic stripping and cleaning composition consisting essentially of:

a) about 55 to 85% by weight of a polyhydric alcohol having the formula selected from the group consisting of HO[CH<sub>2</sub>—CH<sub>2</sub>O]<sub>n</sub>H and



more;

b) about 5 to 35% by weight of a water soluble organic polar solvent;

c) about 0.5 to 20% by weight of ammonium fluoride;

d) an effective amount of up to about 20% by weight total for acetic acid and ammonium acetate; and

e) the remainder being water; said composition having a pH greater than 4 and less than 7.

2. The composition of claim 1 wherein said polyhydric alcohol is propylene glycol.

3. The composition of claim 1 further consisting essentially of a corrosion inhibitor.

4. The composition of claim 3 wherein said inhibitor is selected from the group consisting of catechol, pyrogallol, gallic acid and anthranilic acid.

5. The composition of claim 1 wherein said polar solvent is selected from the group consisting of dimethylsulfoxide, dimethylacetamide, N-methylpyrrolidone and gamma butyrolactone.

6. The composition of claim 1 with dimethylsulfoxide, ammonium fluoride, propylene glycol, a corrosion inhibitor and water.

7. The composition of claim 6 further consisting essentially of a phosphate buffer.

8. A process for stripping and cleaning an organic coating from a coated substrate which comprises subjecting said coated substrate to a composition according to claim 6 at an elevated temperature for a stripping effective time.

9. A process for stripping and cleaning an organic coating from a coated substrate which comprises subjecting said

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coated substrate to a composition according to claim 7 at an elevated temperature for a stripping effective time.

10. The composition of claim 1 further consisting essentially of a phosphate buffer.

11. A process for stripping and cleaning an organic coating from a coated substrate which comprises subjecting said coated substrate to a composition according to claim 1 for a period of time to strip organic material from said substrate.

12. The process of claim 11 wherein said process is conducted at a temperature between about ambient to 80° C.

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13. The process of claim 12 wherein said coated substrate is a photoresist.

14. A process for stripping and cleaning an organic coating from a coated substrate which comprises subjecting said coated substrate to a composition according to claim 3 for a stripping effective time.

15. The process of claim 14 wherein said process is conducted at a temperature between about ambient to 80° C.

\* \* \* \* \*

[54] ETCHANT SOLUTION CONTAINING  
HF-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> FOR ETCHING  
AL-TI-CU OR NI CONTACT METALLURGY  
ON SILICON SUBSTRATES

[75] Inventor: Mark A. Spak, Edison, N.J.

[73] Assignee: RCA Corporation, New York, N.Y.

[21] Appl. No.: 904,541

[22] Filed: May 10, 1978

[51] Int. Cl.<sup>2</sup> ..... H01L 21/44; H01L 21/88;  
H01L 21/465

[52] U.S. Cl. .... 430/318; 156/657;  
156/664; 156/665; 156/666; 156/656; 252/79.3;  
430/316; 430/323

[58] Field of Search ..... 252/79.3; 156/656, 657,  
156/664, 665, 666; 79.4; 357/71; 96/36

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Primary Examiner—Jerome W. Massie

Attorney, Agent, or Firm—Birgit E. Morris; Howard F. VanDenburgh

[57]

#### ABSTRACT

An etchant solution for multilayered metal layers comprising an aqueous solution of from 0.5 to 50 percent by weight of nitric acid, from 0.03 to 1.0 percent by weight of hydrofluoric acid, from 0.05 to 0.5 percent by weight of hydrogen peroxide and from 0.1 to 1.0 percent by weight of sulphuric acid. The solution is compatible with photolithographic techniques and uniformly etches three or more metals.

5 Claims, No Drawings

# ETCHANT SOLUTION CONTAINING HF-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O<sub>2</sub> FOR ETCHING AL-TI-CU OR NI CONTACT METALLURGY ON SILICON SUBSTRATES

This invention relates to an etchant for multilayered metals. More particularly this invention relates to an etchant for various metals which etches them at similar etch rates.

## BACKGROUND OF THE INVENTION

In the manufacture of power devices such as silicon controlled rectifiers, horizontal deflector transistors and the like, several metal layers are applied over glass or silicon surfaces. These metals must be etched away in predetermined places to reveal the substrate beneath. Since metals generally etch at different rates in a single etchant, in order to closely control the process, a different etchant can be employed for each metal present; however, this is a cumbersome and expensive process.

It would be desirable to have a single etchant which can etch several metals at similar rates. However, the requirements for such an etchant are stringent. A single etchant solution must be able to etch different metals at about the same rate across the whole surface of the coated substrate; that is, the etch rate should be uniform at the edges and across the surface of the device, as well as for the different metals to be etched. The etchant must also avoid undercutting the layers. That is, a good etchant will minimize interaction between the various metals which would cause undercutting of the various metal layers. In addition, the etchant must be compatible with conventional photolithographic techniques. The etchant should not attack the photoresist coating or cause a loss of adhesion of the photoresist to the metal layer beneath which would cause undue undercutting and loss of resolution of the desired pattern. Finally, the etchant should not adversely affect the exposed substrate.

## SUMMARY OF THE INVENTION

The etchant solution of the invention comprises from about 0.5 to about 50 percent by weight of nitric acid; from about 0.03 to 1.0 percent by weight of hydrofluoric acid, from about 0.05 to 0.5 percent by weight of hydrogen peroxide, and from about 0.1 to 1.0 percent by weight of sulphuric acid in an aqueous solution. A surface active agent can be added to improve the wetting properties of the solution. This etchant etches various metals at a uniform rate; is compatible with conventional photoresists; does not promote interaction between the metals during etching; and has minimal effect on insulating substrates.

## DETAILED DESCRIPTION OF THE INVENTION

Various power devices comprise three or more layers of metal over an insulating substrate. These metals may include aluminum as a first layer which gives a good bond to the substrate; titanium, molybdenum or tungsten as the second layer; these metals adhere to aluminum and act as a barrier layer to prevent diffusion of nickel or copper into the substrate and prevent reaction of these metals to the aluminum; and nickel or copper as the third layer. These latter metals give good contact to titanium for example, and are solderable metals. A fourth layer of copper can be put down between the

nickel and the titanium, or, alternatively, layers of nickel and copper can be alternated as the third layer.

The thicknesses of these layers can vary from about 0.1 to 8 microns for the aluminum layer; from about 0.2 to about 0.7 micron for the second layer and from about 0.4 to 2 microns for the third layer. These layers are applied to the substrate using conventional evaporation techniques.

The substrate can be glass or other silicon-containing material such as silicon, doped silicon, polycrystalline silicon whether undoped or doped with oxygen for example, silicon oxide or silicon nitride.

In preparing electronic devices such as power devices, a substrate is covered with the multilayers of metal and then coated with a photoresist. The photoresist is exposed to light of an appropriate wavelength through a mask, which changes the solubility of the resist. The resist is developed in a suitable solvent which dissolves the more soluble portions to reveal the underlying metal layers in a pattern of resist and metal. The metal is then etched away with an etching solution to reveal the substrate beneath. The photoresist can then be removed, leaving a pattern of metal and substrate material.

The present etchant solution give excellent control of the etch rate for various metals independent of their position on the substrate and does not promote interaction between different metals such as aluminum and nickel. Although the etch rates for aluminum alone or nickel alone in the etchant are very different, the rates of dissolution are changed when the metals are together in the etchant, such that the etch rates for the different metals are similar.

The temperature of the etchant solution during etching is important and should be maintained between about 25 to about 65° C., preferably from about 48° to 52° C.

The etchant solution of the invention is made by adding the acids and hydrogen peroxide to water and mixing. A small amount of a surface active agent which is stable in acidic solution is optionally added to improve the wetting properties of the etchant to the metal layers. A minimum amount of surfactant is employed; an amount sufficient to change the wetting properties of the solution, but an amount insufficient to dilute the acid content of the solution.

The invention will be further described by the following Examples but the invention is not meant to be limited to the details expressed therein. In the Examples parts are by weight.

## EXAMPLE 1

Silicon wafers which were doped to define N and P type regions therein were coated first with a layer of aluminum about 3 microns thick, then with a layer of titanium about 0.3 micron thick to act as a barrier layer with respect to a succeeding layer of nickel about 0.7 micron thick.

The coated wafers were covered with Waycoat SC photoresist and baked at 150° to 160° C. for 1.5 hours. The resist was exposed through a mask and developed to form a desired pattern of resist and metal.

The wafers were then immersed in an etchant solution maintained at about 50° C. for 16 to 20 minutes. The etchant solution was made by mixing 24 parts of 70 percent nitric acid in 1960 parts of water, adding 2 parts of 40 percent hydrofluoric acid, 9 parts of 30 percent

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hydrogen peroxide, 4 parts of 97 percent sulphuric acid and 1 part of Tergitol surfactant.

Excellent pattern definition was obtained with little undercutting and all of the unprotected metal was removed.

#### EXAMPLE 2

Doped silicon wafers were passivated with a layer of polycrystalline, oxygen-doped silicon and coated with three metal layers and lithographically patterned as in Example 1. The wafers were immersed in the etchant solution of Example 1 for 20 minutes until the bared metal was removed.

The surface of the exposed polycrystalline silicon passivation layer was examined under a microscope. No damage to this layer was noted.

I claim:

1. A method of etching three or more metal layers on a silicon-containing substrate using a single etchant which comprises applying a photoresist over the metal layers, exposing the photoresist through a mask, developing the photoresist to reveal portions of the metal layers and immersing the wafer in an etchant solution comprising from about 0.5 to 50 percent by weight of nitric acid, from about 0.03 to 1 percent by weight of hydrofluoric acid, from about 0.05 to 0.5 percent by

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weight of hydrogen peroxide and from about 0.1 to 1.0 percent by weight of sulphuric acid until the metal not covered by photoresist has dissolved.

2. A method according to claim 1 wherein said metal layers comprise a first layer of aluminum from about 0.1 to 8 microns thick; a second layer of titanium, molybdenum or tungsten from about 0.2 to 0.7 micron thick; and a third layer selected from the group consisting of nickel and copper or both from about 0.4 to 2 microns thick.

3. A method according to claim 1 wherein said silicon-containing substrate is selected from the group consisting of silicon; doped silicon, polycrystalline silicon, oxygen-doped polycrystalline silicon, silicon oxide and silicon nitride.

4. A method according to claim 1 wherein the substrate is a silicon wafer, the metal layers are aluminum about 3 microns thick, titanium about 0.3 micron thick and nickel about 0.7 micron thick.

5. A method according to claim 1 wherein the substrate is a polycrystalline, oxygen doped silicon over a doped silicon wafer and the metal layers are aluminum about 3 microns thick, titanium about 0.3 micron thick and nickel about 0.7 micron thick.

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**United States Patent** [19]  
**McClean**

[11] **Patent Number:** **4,462,861**  
[45] **Date of Patent:** **Jul. 31, 1984**

[54] **ETCHANT WITH INCREASED ETCH RATE**

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[73] **Assignee:** **Shipley Company Inc., Newton, Mass.**

[21] **Appl. No.:** **551,037**

[22] **Filed:** **Nov. 14, 1983**

[51] **Int. Cl.<sup>3</sup>** ..... **C23F 1/02; B44C 1/22; C03C 15/00; C03C 25/06**

[52] **U.S. Cl.** ..... **156/640; 156/659.1; 156/666; 252/79.4**

[58] **Field of Search** ..... **252/79.2, 79.4, 142; 156/640, 659.1, 666; 134/3, 41**

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*Attorney, Agent, or Firm*—Dike, Bronstein, Roberts, Cushman & Pfund

[57] **ABSTRACT**

A process for etching copper comprising contact of the copper with an etchant that is an aqueous solution of sulfuric acid, a peroxide and a low molecular weight carboxylic acid. The low molecular weight carboxylic acid in the etchant exalts etch rate.

**27 Claims, No Drawings**

## ETCHANT WITH INCREASED ETCH RATE

## BACKGROUND OF THE INVENTION

## 1. Introduction

This invention relates to an etchant comprising sulfuric acid activated with hydrogen peroxide and characterized by an enhanced etch rate. The etchant is particularly useful in the manufacture of printing circuit boards.

## 2. Description of the Prior Art

The activation of relatively dilute mineral acids with an oxygen release compound is known in the art and described, for example, in *Plating "Surface Treatment of Metals with Peroxygen compounds"*, Vol. 42, p. 561 (1955). In the *Plating* publication, it is taught that mineral acids such as sulfuric acid, nitric acid, acetic acid and phosphoric acid may be activated with oxygen release compounds such as hydrogen peroxides or other peroxy, persulfate or perborate compounds. The oxygen release compounds enhance the etch rate thereby permitting a decrease in the concentration of the acid.

Activation of dilute sulfuric acid with hydrogen peroxide is most attractive due to low cost and ease of electrolytic copper recovery from the spent etchant prior to disposal. However, the utility of hydrogen peroxide etching solutions is reduced somewhat due to catalyzed decomposition of hydrogen peroxide caused by etched metal ions or other transition metal ions in solution and a slow etch rate, typically 1.4 mils of copper from 1 ounce copper clad laminate in 10-25 minutes at 120° F. To enhance or exalt etch rate, more concentrated solutions of hydrogen peroxide have been used, but concentrated peroxide solutions are hazardous to health and safety. In addition, such etchants have not been successfully used with tin dissimilar metal etch resists because they attack tin, especially immersion tin.

In U.S. Pat. No. 4,130,454, incorporated herein by reference, a modified peroxide etch is disclosed and claimed. The etchant comprises hydrogen peroxide and a molybdenum compound in an acidic solution. The hydrogen peroxide provides a sustained etch rate and the molybdenum etches at a substantially greater rate than the peroxide thereby exalting the rate to a desired level for commercial use. Molybdenum cannot be used as a sole oxidant because it is rapidly depleted due to reduction to a lower valence form as etching proceeds. It is therefore incapable of providing sustained etching. Patentee proposes a theory that the combination of peroxide and molybdenum is a synergistic combination because both are believed to etch the peroxide in the acid environment while providing the secondary function of oxidizing molybdenum to a higher valence capable of etching metals in the acidified environment.

The peroxide etchants described above are used to etch copper both by immersion and by spraying. Immersion etching comprises immersing a part within the etchant until the desired amount of metal is dissolved. Spray etching comprises spraying a finely divided stream of etchant against the surface of the part until the desired amount of metal is dissolved. Spray etching generally provides the advantage of a more rapid etch rate because the finely divided droplets of etchant are aerated resulting in additional oxygen at the surface of the part being etched and a concomitant increase in etch rate.

The etchants of the aforesaid U.S. Pat. No. 4,130,454 do provide the exalted etch rate as reported in the pa-

tent for immersion etching. However, for spray etching, the etch rate appears to be retarded rather than exalted which is contrary to that which would be expected. Consequently, the etchant of said patent is usable for spray etching, but spray etching of said etchant may not be commercially practical where high through put of parts is required.

## SUMMARY OF THE INVENTION

The invention described herein is a peroxide etchant especially useful for rapidly dissolving large quantities of copper containing metals—i.e., copper and its alloys. The etchant is characterized by an exalted etch rate when used in both the immersion and spray modes. For immersion etching, the etchant of the invention has an etch rate comparable to the etchants of the aforesaid patent utilizing molybdenum as the exaltant and are able to dissolve all of the copper from a one ounce copper clad circuit board base material in from about 6 to 8 minutes, dependent upon the specific formulation used. For spray etching, the etchants are capable of dissolving all of the copper from one ounce copper clad base material in about 1.5 to 3 minutes compared to from about 10 to 15 minutes for those etchants using molybdenum as the exaltant.

In accordance with the invention, increased etch rate is achieved by the addition of a low molecular weight carboxylic acid to a peroxide etchant in sufficient quantity to increase the etch rate to the desired level. The carboxylic acid provides a secondary advantage of stabilizing the etchant against peroxide decomposition.

The etchants of the invention are used primarily as a final etch to dissolve large quantities of copper such as in chemical milling and printed circuit board manufacture.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

For purposes of definition herein, the term etchant is used in its art recognized sense as a solution to remove substantial quantities of metal from a metal surface (description from *The Language of Printed Circuits*, PC FAB, July, 1982, Pg. 60) as contrasted to a pickling solution that is used to remove contaminants from the surface of a metal such as oxides and scales (description from *Finishing Handbook and Directory 1979*, edited by Capp, Sawell Publications Ltd., London, P. 891).

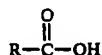
Though acids other than sulfuric acid may be used as a source of acidity for the etchants of the invention, sulfuric acid is preferred because it is the most economical, provides best results and yields copper sulfate upon saturation which is readily recovered by lowering the temperature of the etchant. Other acids may be used in admixture with the sulfuric acid for specific results. Therefore, the term sulfuric acid as used herein means sulfuric acid alone or mixed with other acids in lesser amounts where desired.

The concentration of the acid in the etchant may vary within broad limits but preferably, the acid content of the etchant is relatively low varying between about 0.1 and 2.5 Normal and preferably between about 0.5 and 1.5 Normal.

The peroxide content of the etchant may also vary within relatively broad limits such as from 0.1 to 10 moles per liter of solution. However, because peroxide is a relatively dangerous material to handle, its concentration is preferably maintained relatively low and pref-

erably within the range of between about 0.5 and 2.5 moles per liter. As the peroxide content drops below 0.3 moles per liter, the etch rate begins to decrease.

The exaltant is a low molecular carboxylic acid conforming to the following general formula:



where R is hydrogen or a lower alkyl group having from 1 to 6 carbon atoms. Examples of suitable acids include acetic acid, propionic acid and butyric acid. Of the carboxylic acids encompassed by the above formula, propionic acid is preferred.

The concentration of the carboxylic acid can vary within broad limits. In all cases, the amount is sufficient to exalt the rate, preferably to a rate double the rate of etch absent the acid. This amount can vary from 0.1 to 2.0 moles per liter of etchant and amounts of from about 0.3 to 1 mole per liter are preferred.

Peroxide etchants are typically stabilized to prevent catalytic decomposition of the peroxide caused by metal impurities. The exaltants of the invention function as stabilizers. If desired, other stabilizers known to the art may be added such as the aylsulfonic acids or salts thereof as disclosed in U.S. Pat. No. 3,801,512. In this patent, a preferred stabilizer is phenol sulfonic acid. Other stabilizers include sulfosalicylic acid and toluene sulfonic acid. The concentration of the stabilizer, if used, may vary from as low as 1 gram per liter of solution to the solubility limit of the acid, but preferably varies between about 3 and 30 grams per liter of solution.

Another additive that may be added to the etchant of the invention is a source of phosphate ions used as an inhibitor to prevent attack on tin, especially immersion tin, as well as several other metals such as nickel and alloys of nickel such as gold alloys. The use of phosphate ions as an inhibitor in such etchants is disclosed in U.S. Pat. No. 4,144,119. The concentration of the phosphate ion in the etchant is not critical, minor amounts inhibiting attack on tin to some degree and larger amounts providing greater protection. This amount may vary between about 0.1 and 2.5 moles per liter (as phosphate) and more preferably, between about 0.25 and 1.5 moles per liter, all as taught in the aforesaid patent.

Using the etchants of this invention to etch copper at 120° F., the bath will dissolve from about 70 to 80 grams of copper per liter assuming the hydrogen peroxide concentration is maintained between 50 and 100% of its initial makeup. Allowing the bath to cool to room temperature induces crystallization of copper compounds which may be recovered by filtration dependent upon the acid used. When sulfuric acid is used as the source of acidity, relative pure copper sulfate crystals may be recovered. Readjustment in the concentration of the components comprising the etch solution makes the same suitable for re-use.

The etchants of the invention are used for the same purposes as similar etchants of the prior art. They are particularly used for the manufacture of printed circuit boards and for chemical milling. Procedures for the formation of printed circuit boards are described in numerous publications, for example, in Coombs, *Printed Circuits Handbook*, McGraw-Hill Publishing Company,

New York, 1967, Chapter 5, incorporated herein by reference.

In a typical process for the manufacture of a printed circuit board, a suitable base material is selected such as copper clad epoxy. Holes are drilled at appropriate locations on the board and the walls of the holes are metallized with copper to provide electrical contact between the two surfaces of the base material. Methods for metallization are known and include the steps of cleaning, catalyzing and electroless copper deposition.

Following metallization of the holes, utilizing a process known as pattern plating, a conductor pattern is formed on the copper by application of an organic resist material which may be either a photoresist or a screen resist, dependent upon the design and definition of the board. The resist coats the copper that is not part of the conductor pattern and leaves the copper bare in a conductor pattern. Thickness of the copper pattern is then increased by electrolytic copper plating. Following copper plating, a dissimilar metal etch resist such as solder may be applied over the copper in the conductor pattern to protect the same from subsequently applied etchants, the organic resist is removed exposing the unwanted copper (not part of the conductor pattern), and the unwanted copper is dissolved with a suitable etchant for the copper such as that disclosed herein while the conductor pattern is protected from the etchant by the dissimilar metal etch resist. Typically, the dissimilar metal etch resist is selected not only for its ability to withstand the etchant, but also for its solderability so that electrical connections can be soldered directly to the etch resist.

The invention will be better understood by reference to the following examples:

#### EXAMPLES 1 THROUGH 9

Sulfuric acid (50%) ml	163.0
Phosphoric acid (50%) ml	50.0
Surfactant gm	0.3
Copper sulfate.5H <sub>2</sub> O <sup>1</sup> gm	116.1
Hydrogen peroxide (50%) ml	50.0
Propionic acid (100%) ml	variable
Water	to 1 liter

<sup>1</sup>Copper sulfate added to simulate commercial conditions of use.

The above etchants were used to etch copper from a 1 ounce copper clad epoxy substrate (1.4 mil thick copper) by immersion in the etchant maintained at 120° F. until all of the copper was removed. The amounts of propionic acid used and the results obtained (average of three samples) are set forth in the following table:

Example No.	Amount (ml) Propionic acid	Time (min.)
1.	0	17.7
2.	10	12.7
3.	21	9.7
4.	31	6.7
5.	42	4.4
6.	52	6.7
7.	62	7.1
8.	83	6.4
9.	104	3.0

#### EXAMPLES 10 AND 11

Sulfuric acid (50%) ml	163.0
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-continued

Phosphoric acid (50%) ml	50.0
Phenol sulfonic acid gm	1.0
Copper sulfate.5H <sub>2</sub> O <sup>1</sup> gm	75.1
Hydrogen peroxide (50%) ml	50.0
Propionic acid (100%) ml	variable
Water	to 1 liter

<sup>1</sup>Copper sulfate added to simulate commercial conditions of use. In example 11, the copper sulfate concentration was at 89.9 grams per liter.

The epoxy substrates of examples 1 to 10 were used for these examples, but etching was by spraying at 120° F. rather than by immersion. Without the propionic acid, it took 18.4 minutes to remove the copper. With 53 ml per liter of propionic acid, the etch time was reduced to 3 minutes.

## EXAMPLE 12

The procedure of examples 10 and 11 was repeated substituting acetic acid for propionic acid. The acetic used was a 98% solution and added in an amount of 40 ml per liter. With a fresh etchant, the spray time was 20 minutes. After 20 minutes of use, the spray time was 5.5 minutes indicating that an aging process of some sort might be necessary for acetic acid.

A printed circuit board may be prepared from copper clad epoxy substrate using the following sequence of steps:

- Clean the substrate and drill holes at appropiate locations.
- Metallize the walls of the holes by electroless plating including the steps of catalysis with a catalyst such as catalyst 6F of Shipley Company Inc., accelerate with a mild acid solution and electrolessly plate copper such as with copper mix CP-74 of Shipley Company Inc.
- Apply a positive working photoresist such as Microposit 1350, expose and develop.
- Electroplate copper to full desired thickness.
- Apply immersion tin over the exposed copper.
- Remove the photoresist by dissolution in a suitable solvent.
- Remove exposed copper by immersion of the circuit board in the etchant of example 9 until all unwanted copper is dissolved.

I claim:

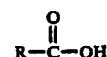
- A process for the manufacture of a printed circuit board comprising the step of contacting a copper clad printed circuit board base material, having an etch resist over the surface of the copper defining a circuit pattern, with an etchant for a time sufficient to remove all exposed copper, said etchant comprising an aqueous solution of a peroxide and sulfuric acid, each in an amount sufficient to provide a sustained rate of etching, and propionic acid in an amount sufficient to exalt the etch rate to a rate in excess of that achievable by the peroxide-sulfuric mixture alone.
- The process of claim 1 where the propionic acid is present in an amount sufficient to double the etch rate relative to said etchant free of the carboxylic acid.
- The process of claim 1 where the peroxide content varies between about 0.5 and 2.5 moles per liter.
- The process of claim 1 where the concentration of the propionic acid ranges from about 0.1 to 2.5 moles per liter of solution.
- A process for dissolving a copper containing metal comprising contact of the copper metal with an etchant that is an aqueous solution of a peroxide and sulfuric acid, each in amounts sufficient to provide a sustained

rate of etching of the copper metal, and a low molecular weight carboxylic acid in an amount sufficient to exalt the etch rate to a rate at least double that achievable with the peroxide-sulfuric mixture alone.

- The process of claim 5 where the copper metal is contacted with the etchant for a time sufficient to dissolve a copper layer having a thickness of at least 0.1 mils.

- The process of claim 5 where the peroxide content varies between 0.5 and 2.5 moles per liter.

- The process of claim 6 where the carboxylic acid conforms to the general formula:



where R is hydrogen or alkyl having from 1 to 6 carbon atoms.

- The process of claim 8 where the carboxylic acid is propionic acid.

- The process of claim 5 where the carboxylic acid is present in an amount of from 0.1 to 2.5 moles per liter of solution.

- The process of claim 6 where the contact of the copper metal is by immersion of the copper metal in a solution of the etchant.

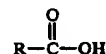
- The process of claim 6 where the contact of the copper metal is by spraying the etchant onto the surface of the copper metal.

- A process for the manufacture of a printed circuit board comprising the step of contacting a copper clad printed circuit board base material, having an etch resist over the surface of the copper defining a circuit pattern, with an etchant for a time sufficient to remove all exposed copper, said etchant comprising an aqueous solution of a peroxide and sulfuric acid, each in an amount sufficient to provide a sustained rate of etching, and a low molecular weight carboxylic acid in an amount sufficient to exalt the etch rate to a rate in excess of that achievable by the peroxide-sulfuric mixture alone.

- The process of claim 13 where the carboxylic acid is present in an amount sufficient to double the etch rate relative to said etchant free of the carboxylic acid.

- The process of claim 13 where the peroxide content varies between about 0.5 and 2.5 moles per liter.

- The process of claim 15 where the carboxylic acid conforms to the general formula:



where R is hydrogen or alkyl having from 1 to 6 carbon atoms.

- The process of claim 16 where the carboxylic acid is propionic acid.

- The process of claim 13 where the concentration of the carboxylic acid ranges from about 0.1 to 2.5 moles per liter of solution.

- The process of claim 13 where the etch resist is solder or immersion tin.

- The process of claim 19 where the etchant contains a solution soluble phosphate.

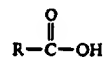
- The process of claim 13 where the contact of the printed circuit board base material is by immersion in a solution of the etchant.

22. The process of claim 13 where the contact of the circuit board base material is by spraying the etchant onto the surface of the printed circuit board base material.

23. A process for exalting the etch rate of a hydrogen peroxide-sulfuric acid etchant, said process comprising adding a low molecular weight carboxylic acid to the etchant in a concentration sufficient to double the etch rate compared to an etchant free of the carboxylic acid.

24. The process of claim 23 where the peroxide content varies between 0.5 and 2.5 moles per liter.

25. The process of claim 23 where the carboxylic acid conforms to the general formula



where R is hydrogen or alkyl having from 1 to 6 carbon atoms.

26. The process of claim 25 where the carboxylic acid is propionic acid.

27. The process of claim 26 where the carboxylic acid is present in an amount of from 0.1 to 2.5 moles per liter of solution.

\* \* \* \* \*



US005851303A

**United States Patent** [19]  
**Hwang et al.**

[11] **Patent Number:** **5,851,303**  
 [45] **Date of Patent:** **Dec. 22, 1998**

[54] **METHOD FOR REMOVING METAL  
 SURFACE CONTAMINANTS FROM SILICON**

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[21] **Appl. No.:** **642,137**

[22] **Filed:** **May 2, 1996**

[51] **Int. Cl.<sup>6</sup>** ..... **B08B 7/04**

[52] **U.S. Cl.** ..... **134/3; 134/2; 134/26;**  
 134/28; 134/30; 436/177

[58] **Field of Search** ..... 134/2, 3, 26, 28,  
 134/30; 216/59, 73, 74, 79; 438/704; 436/177

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*Attorney, Agent, or Firm*—Richard I. Gearhart

[57] **ABSTRACT**

A method for removing metal surface contaminants from  
 silicon metalloid. The method comprises sequentially con-  
 tacting the silicon with gaseous hydrogen fluoride and then  
 with an aqueous solution comprising at least one-half weight  
 percent hydrogen peroxide. The method is especially useful  
 as a means for recovering metal surface contaminants on  
 semiconductor grade silicon for analysis of surface contami-  
 nation of the silicon by such metals. The method is useful for  
 recovering copper from the surface of semiconductor grade  
 silicon in an aqueous solution which can be analyzed  
 directly to determine the amount of copper contamination of  
 the surface of the silicon.

**20 Claims, No Drawings**

## METHOD FOR REMOVING METAL SURFACE CONTAMINANTS FROM SILICON

### BACKGROUND OF INVENTION

The present invention is a method for removing metal surface contaminants from silicon metalloid. The method comprises sequentially contacting the silicon with gaseous hydrogen fluoride and then with an aqueous solution comprising at least one-half weight percent hydrogen peroxide. The method is especially useful as a means for recovering metal surface contaminants on semiconductor grade silicon for analysis of surface contamination of the silicon by such metals. The method is useful for recovering copper from the surface of semiconductor grade silicon in an aqueous solution which can be analyzed directly to determine the amount of copper contamination on the surface of the silicon.

The production of high density integrated circuits requires wafers of monocrystalline silicon of high purity. Metal contaminants of the silicon including, among others, copper, gold, iron, cobalt, nickel, chromium, tantalum, zinc, tungsten, titanium, magnesium, molybdenum, and aluminum can be harmful to the production of such integrated circuits. These impurities, even in small amounts, may introduce defect sites in the semiconductor grade material which can ultimately result in degraded device performance and limited circuit density. Therefore to control the quality of silicon intended for use in the semiconductor industry, methods for cleaning silicon as well as accurate methods for determining metals contamination of the surface are desired.

Methods for surface cleaning of silicon used in semiconductor devices are well known in the art. Such methods are described in Iscoff (Editor), *Semiconductor International*, July, 1993, pages 58-63, and include a method typically referred to as the "RCA" method. The RCA method comprises cleaning the silicon with an aqueous  $\text{H}_2\text{O}_2\text{--NH}_4\text{OH}$  and an aqueous  $\text{H}_2\text{O}_2\text{--HCL}$  mixture at  $75^\circ\text{C}$ . to  $80^\circ\text{C}$ . for 10 minutes. Burggraaf (Editor), *Semiconductor International*, October, 1990, pages 52 to 58, further discusses such cleaning techniques. Burggraaf states that although a HF-vapor process can remove native oxide layers, these processes cannot effectively remove metallic contaminants because most metals do not generate volatile species with appreciable vapor pressure. Burggraaf further states that an integral deionized water rinse following exposure to vapor-phase HF cleaning can remove soluble metallic species.

Park et al., *J. Electrochem. Soc.*, Vol. 142(No.2), pages 571 to 576, describe the use of aqueous solutions comprising  $\text{HF--H}_2\text{O}$ ,  $\text{HNO}_3\text{--HF--H}_2\text{O}$ , or  $\text{HNO}_3\text{--HF--H}_2\text{O}_2$  for cleaning silicon. Park et al. also describe the use of aqueous  $\text{HF--H}_2\text{O}_2$  systems for cleaning silicon.

Niwayama et al., JP (Heisei) 5-4811, describe the treatment of silicon with an aqueous solution of hydrogen fluoride and hydrogen peroxide. The solution comprises by volume one portion of a 50 weight percent aqueous solution of hydrogen fluoride, 0.03 to 4 portions of a 31 weight percent hydrogen peroxide solution, and one to ten portions of water.

In a preferred embodiment of the present invention metal surface contaminants are recovered from semiconductor grade silicon in an aqueous solution, which is then analyzed by standard analytical techniques to quantify the amount of metal surface contamination of the semiconductor grade silicon. The present method offers an advantage over wet methods currently used in the art for cleaning silicon metalloid by not requiring large volumes of aqueous hydrogen

fluoride. Another advantage of the present method is the ability to remove metal oxides and metals bonded directly to silicon, such as copper, from the surface of the silicon. The present method allows for essentially quantitative recovery of metal surface contaminants, such as copper, in aqueous solution from the surface of semiconductor grade silicon, and thereby provides a convenient solution for analysis of the concentrations of the removed metals.

### SUMMARY OF INVENTION

The present invention is a method for removing metal surface contaminants from silicon metalloid. The method comprises sequentially contacting the silicon with gaseous hydrogen fluoride and then with an aqueous solution comprising at least one-half weight percent hydrogen peroxide. The method is especially useful as a means for recovering metal surface contaminants on semiconductor grade silicon for analysis of surface contamination of the silicon by such metals. The method is useful for recovering copper from the surface of semiconductor grade silicon in an aqueous solution which can be analyzed directly to determine the amount of copper contamination of the surface of the silicon.

### DESCRIPTION OF INVENTION

The present invention is a method for removing metal contaminants from the surface of silicon metalloid. The method comprises

- (A) in a first step contacting silicon metalloid having a metal surface contaminant with vapor phase hydrogen fluoride and
- (B) in a second step contacting the silicon metalloid having the metal surface contaminant with an aqueous solution comprising at least one-half weight percent hydrogen peroxide.

The silicon metalloid (herein referred to as "silicon") from which metal surface contaminants can be removed by the present method is not limiting and can generally be any composition comprising at least 95 percent by weight of elemental silicon. A preferred silicon for use in the present invention is semiconductor grade silicon. By "semiconductor grade" silicon, it is meant a material comprising at least 99 percent by weight silicon. The physical shape of the silicon is not critical to the present invention and can be in the form of rods, wafers, chunks, and particles. The present method is especially useful for removing metal surface contaminants from silicon chunks intended for use in a process such as the Czochralski method for forming monocrystalline silicon from a melt.

In the first step of the present process, the silicon having a metal surface contaminant is contacted with hydrogen fluoride in the vapor phase. The method of contacting the silicon with the hydrogen fluoride is not critical to the present invention. It is preferred that the contact be effected in a closed vessel formed from a non-contaminating material such as Teflon® (E.I. du Pont de Nemours and Co., Wilmington, Del.). The hydrogen fluoride can be provided to the vessel either initially in the gaseous phase or as a saturated aqueous solution from which the gaseous hydrogen fluoride is evolved. Preferred is when the hydrogen fluoride is provided to the vessel as an aqueous solution from which the gaseous hydrogen fluoride then evolves. An advantage of the present invention is that it does not require large quantities of aqueous hydrogen fluoride to be effective. It is not necessary to provide the aqueous hydrogen fluoride to the vessel in a quantity sufficient to wet the surface of the silicon or to effect a rinse of the silicon. It is preferred to use

volumes of aqueous hydrogen fluoride which are insufficient to wet the surface of the silicon in the vessel. Typically about 0.5 ml to 5 ml of a 50 weight percent aqueous hydrogen fluoride solution, or the equivalent thereof, per each 250 ml of container volume is considered useful in the present method. The weight and surface area of the silicon sample is not particularly critical and can be varied within wide limits. An example of a useful weight of silicon and a physical form is provided in the examples herein.

The silicon can be contacted with the hydrogen fluoride vapor at a temperature within a range of about 15° C. to 100° C. Preferred is when the silicon is contacted with the hydrogen fluoride vapor at a temperature within a range of about 20° C. to 30° C. The required length of time of contact of the silicon with the hydrogen fluoride vapor will depend to a great extent on the temperature at which the contact is effected. Generally the contact time should be at least ten minutes. Preferred is when the contact time is at least one hour and the contact temperature is within a range of about 20° C. to 30° C.

In a second step of the present method the silicon having the metal surface contaminant is contacted with an aqueous solution comprising at least one-half weight percent hydrogen peroxide. The weight percent hydrogen peroxide as used herein means the weight percent of hydrogen peroxide in the final weight of water with which the silicon is contacted. Therefore, if an aqueous solution of hydrogen fluoride is used in the first step the volume of water added during this first step would be considered as part of the total water present in the method. It is not necessary that the residual aqueous solution of hydrogen fluoride be present during conduct of the second step. However, a portion of the metal surface contaminants present on the silicon may be removed during this step and should be accounted for in any subsequent analysis.

In the present method it is preferred that the aqueous solution comprise about one to 10 weight percent hydrogen peroxide. Even more preferred is when the aqueous solution comprises about 1.5 to five weight percent hydrogen peroxide. Higher concentrations of hydrogen peroxide may be used if desired.

A sufficient volume of the aqueous solution comprising at least one-half weight percent hydrogen peroxide should be added in the second step to ensure a complete wetting of the surface of the silicon. Generally, it is preferred that at least 5 ml of the aqueous hydrogen peroxide solution be present in the method per each 100 g of silicon. Even more preferred is when at least 10 ml of the aqueous hydrogen peroxide solution is present in the method per each 100 g of silicon. The upper limit for the amount of aqueous hydrogen peroxide solution that may be added to the present method is defined by the practicality of handling the volume of the resulting aqueous phase, and by dilution considerations if the aqueous phase is to be analyzed for metals. In a preferred method, about 10 ml to 20 ml of aqueous hydrogen peroxide solution is used per each 100 g of silicon.

The temperature at which the silicon is contacted with the aqueous hydrogen peroxide solution is not critical and can generally be within a range of about 15° C. up to the decomposition temperature of the hydrogen peroxide. Preferred is when the silicon is contacted with the aqueous solution of hydrogen peroxide at a temperature within a range of about 20° C. to 30° C. The length of time the silicon is contacted with the aqueous solution of hydrogen peroxide is not critical and can generally be that required to ensure a thorough contact with the surface of the silicon. Generally a contact time of at least one minute is preferred. Even more

preferred is when the silicon is contacted with the aqueous solution of hydrogen peroxide for about one to ten minutes.

The present method is especially useful for removing metal surface contaminants from silicon for determining the amount of such metals on the surface of the silicon. By the term "metal surface contaminants" it is meant any metal or metal compound present on the surface of the silicon. The present method is useful for removing all metals typically found on the surface of semiconductor grade silicon, including transition metals and heavy metals. Metals which may be removed from the silicon include copper, gold, iron, cobalt, nickel, chromium, tantalum, zinc, tungsten, titanium, magnesium, molybdenum, and aluminum. The present method is particularly effective in removing those metals from the surface of silicon where the metal is directly bonded to silicon atoms. Copper is an example of a metal which may be bonded directly to silicon atoms and which can be removed from the surface of silicon by the present method.

In a preferred embodiment of the present invention the aqueous phase containing the metal surface contaminant is analyzed to determine metal concentration. Those skilled in the art will recognize that the silicon may contain more than one metal surface contaminant and consequently the aqueous phase may contain more than one metal contaminant. The method of analyzing the aqueous phase for metal contaminants can be any of those known in the art for such analysis. If desired, the aqueous phase may be dried by evaporation to concentrate or recover the metals as a solid residue for analysis. The aqueous phase may be analyzed for metal content by such methods as graphite furnace atomic adsorption, inductive coupled plasma mass spectrometry, and ion chromatography. In a preferred method, the aqueous phase is analyzed by graphite furnace atomic absorption.

The following examples are provided to illustrate the present invention. These examples are not intended to limit the scope of the claims herein.

#### EXAMPLES

The ability to recover metal contaminants from the surface of semiconductor grade silicon in aqueous solutions consisting essentially of various concentrations of hydrogen peroxide was evaluated. The semiconductor grade silicon was obtained from a standard commercial process for preparing such silicon by chemical vapor deposition. The silicon was broken into pieces of a size such that three to four pieces weighed about 100 grams. Samples of approximately 100 grams of the silicon were placed in 250 ml acid cleaned Teflon® containers for testing. Each silicon sample was acid cleaned by standard wet methods to remove surface contamination. Ten microliters of a standard solution containing 12 ppbw Al (ppbw=parts per billion weight), 6 ppbw Fe, 9 ppbw Zn, 6 ppbw Cu, and 9 ppbw Na were added to each sample.

About 1.5 ml of a 50 weight percent aqueous hydrogen fluoride solution was added to each silicon sample and the Teflon® container was sealed and allowed to set about 18 hours. At the end of the 18 hours, 8.3 ml of a deionized water solution consisting essentially of hydrogen peroxide at a concentration sufficient to provide a final concentration as described in Table 1 was added to the appropriate silicon samples. The hydrogen peroxide was a commercially obtained unstabilized aqueous hydrogen peroxide solution comprising about 31 to 35 weight percent of hydrogen peroxide, diluted in deionized water as required. The final concentration of hydrogen peroxide is based on the total amount of liquid added to the Teflon® container. Approxi-

mately 0.2 ml of concentrated nitric acid was added to the aqueous solution associated with each silicon sample to reduce the potential for evaporation of removed metals during analysis of the solution by graphite furnace atomic adsorption. Each Teflon® container was shaken sufficiently to insure an adequate rinse of the silicon sample.

The resulting aqueous solutions were analyzed for the metals described in Table 1 by graphite furnace atomic absorption. In Table 1 the amount of each metal recovered is reported as a percent of that added by the stock solution, corrected for background as determined by appropriate blanks.

TABLE 1

Effect of H <sub>2</sub> O <sub>2</sub> on Metals Recovery					
Wt. % Metal Recovery					
H <sub>2</sub> O <sub>2</sub> Conc.	Al	Fe	Zn	Cu	Na
0	71	95	93	5	97
0	73	93	110	3	102
0.26	100	113	112	53	101
0.26	108	161	—	65	205
0.87	118	133	94	68	99
0.87	89	115	99	93	98
1.45	125	123	104	105	100
1.45	91	120	102	98	88
2.9	84	107	103	103	93
2.9	103	103	104	128	93

We claim:

1. A method for removing metal surface contaminants from a silicon metalloid, the method comprising:

(A) in a first step contacting silicon metalloid having a metal surface contaminant with vapor phase hydrogen fluoride and

(B) in a second step contacting the silicon metalloid having the metal surface contaminant with an aqueous solution consisting essentially of at least one-half weight percent hydrogen peroxide.

2. A method according to claim 1, where the silicon metalloid is semiconductor grade.

3. A method according to claim 2, where the vapor phase hydrogen fluoride is evolved from a saturated aqueous solution of hydrogen fluoride.

4. A method according to claim 3, where the silicon metalloid is contacted with vapor phase hydrogen fluoride by enclosing the silicon metalloid in a vessel containing a volume of the saturated aqueous hydrogen fluoride solution of about 0.5 ml to 5 ml per each 250 ml vessel volume.

5. A method according to claim 4, where the contact in the first step is effected at a temperature within a range of about 20° C. to 30° C.

6. A method according to claim 1, where the contact in the first step is effected at a temperature within a range of about 15° C. to 100° C.

7. A method according to claim 1, where the aqueous solution of the second step comprises about one to 10 weight percent hydrogen peroxide.

8. A method according to claim 1, where the aqueous solution of the second step comprises about 1.5 to five weight percent hydrogen peroxide.

9. A method according to claim 1, where the contacting of the second step is effected at a temperature within a range of

about 15° C. up to the decomposition temperature of the hydrogen peroxide.

10. A method according to claim 1, where the volume of the aqueous solution of the second step is about 10 ml to 20 ml per each 100 g of silicon metalloid.

11. A method according to claim 1, where the metal surface contaminant is copper.

12. A method for analyzing semiconductor grade silicon for metal surface contaminants, the method comprising:

(A) in a first step contacting semiconductor grade silicon metalloid having a metal surface contaminant with vapor phase hydrogen fluoride,

(B) in a second step contacting the semiconductor grade silicon metalloid with an aqueous solution consisting essentially of at least one-half weight percent hydrogen peroxide thereby forming an aqueous phase containing the metal surface contaminant, and

(C) analyzing the aqueous phase to determine metal concentration.

13. A method according to claim 12, where the silicon metalloid is contacted with vapor phase hydrogen fluoride by enclosing the silicon metalloid in a vessel containing about 0.5 to 5 ml of a saturated aqueous solution of hydrogen fluoride per each 250 ml of vessel volume and the contacting of the first step is effected at a temperature within a range of about 15° C. to 100° C.

14. A method according to claim 12, where the aqueous solution of the second step comprises about one to 10 weight percent hydrogen peroxide.

15. A method according to claim 12, where the aqueous solution of the second step comprises about 1.5 to five weight percent hydrogen peroxide.

16. A method according to claim 12, where the volume of the aqueous solution of the second step is about 10 ml to 20 ml per each 100 g of the silicon.

17. A method according to claim 12, where the contact of the second step is effected at a temperature within a range of about 20° C. to 30° C. for a period of time of about one to ten minutes.

18. A method according to claim 12, where the metal surface contaminant is copper.

19. A method according to claim 12, where the aqueous phase is analyzed by use of graphite furnace atomic adsorption.

20. A method for analyzing semiconductor grade silicon for surface contamination by copper, the method comprising:

(A) in a first step contacting semiconductor grade silicon metalloid having copper as a surface contaminant with vapor phase hydrogen fluoride,

(B) in a second step contacting the semiconductor grade silicon metalloid with about 10 ml to 20 ml per 100 g of silicon of an aqueous solution consisting essentially of about 1.5 to five weight percent hydrogen peroxide thereby forming an aqueous phase containing the copper, and

(C) analyzing the aqueous phase to determine copper concentration by graphite furnace atomic absorption.

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# United States Patent [19]

Acocella et al.

[11] Patent Number: 4,747,907

[45] Date of Patent: May 31, 1988

[54] METAL ETCHING PROCESS WITH ETCH RATE ENHANCEMENT

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[21] Appl. No.: 924,702

[22] Filed: Oct. 29, 1986

[51] Int. Cl.<sup>4</sup> ..... C23F 1/00

[52] U.S. Cl. .... 156/642; 156/664;  
156/666; 134/2; 134/10

[58] Field of Search ..... 156/664, 666, 628, 642,  
156/656; 134/2, 10

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Blecker

## [57] ABSTRACT

A metal etching process involving an oxidation-reduction reaction where the metal being etched is oxidized and the active ingredient in the etchant solution is reduced, incorporates contacting said metal with an etching solution containing an active ingredient selected from the group consisting of ferric ions, ferricyanide ions, ceric ions, chromate ions, dichromate ions, and iodine, and introducing ozone into said etching solution to rejuvenate and agitate the solution.

15 Claims, No Drawings

## METAL ETCHING PROCESS WITH ETCH RATE ENHANCEMENT

### BACKGROUND OF THE INVENTION

This invention is directed to a metal etching process involving contacting a metal with an etching solution containing a metal ion or a complex ion in a first valence state which is reduced to a lower valence state, resulting in oxidizing the metal being etched, thereby forming a metal ion which goes into the solution. More specifically, the invention relates to a process for etching metals that normally have slow etch rates, which process greatly enhances the etch rate of the metals, and provides for rejuvenation of the etching solution.

The general concept of etching metals, particularly copper, with an etchant solution containing an ion in a first valence state that is reduced to a lower valence state by an oxidizing reaction with copper, and forming an ion, is well known and widely used. The process applied to etching copper with ferric chloride solutions is described in U.S. Pat. No. 1,969,678. Various techniques to rejuvenate the etching solution by oxidizing the oxidizing ion in solution back to the original first valence state is well known, as indicated by U.S. Pat. Nos. 2,886,420, 3,600,244, and 3,532,568.

Normally, the etching of copper by such processes proceeds at an acceptable rapid etching rate, particularly with ferric chloride solutions. However, the etching of other metals, for example, nickel, proceeds at an unacceptably slow rate, even though the oxidation potentials for the reactions are thermodynamically favorable. The kinetics of the reaction are intolerably slow for various reasons, some of which are not completely understood. Conceivably some product of an intermediate reaction blocks the metal surface and impedes the overall etching reaction. Agitation from of solution results in only a minor improvement.

### SUMMARY OF THE INVENTION

An object of this invention is to provide an improved process for etching various metals that improves the kinetics of the etching reaction.

Another object of this invention is to provide an improved process for etching metals whereby the reaction rate of the etching reaction is materially increased, and the etching solution is rejuvenated.

Yet another object of this invention is to provide a technique which results in rejuvenation of the etching solution.

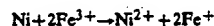
In accordance with the aforementioned objectives, there is provided an improved etching method for etching metals wherein the metal to be etched is contacted with an etchant solution containing as an active ingredient an ion or complex ion having a first valence state that is reducible to a second lower state by the metal, the etchant having an active ingredient selected from the group consisting of, but not limited to, ferric ions, ferricyanide ions, ceric ions, dichromate ions, chromate ions, and iodine while simultaneously introducing ozone into the etching solution to rejuvenate the solution and increase the etching rate of the metal.

### DESCRIPTION OF PREFERRED SPECIFIC EMBODIMENTS

There are many applications, in particular in the electronics industry, where there is a pressing need to etch relatively thick layers of metals. In a manufacturing

environment it is essential that the etching proceed at a rapid rate in order that the etching process will be economically feasible. A typical example of such a need for etching thick metal layers is in the forming of interconnection decals for joining semiconductor devices to electrical networks on supporting substrates.

Nickel is a desirable metal for this purpose. When it is exposed to a ferric chloride solution, however, it may require up to six hours in the bath at room temperature, which is unacceptable throughput in a manufacturing environment. While an aqueous ferric chloride solution etches copper quite rapidly, it does not do the same for nickel. Although the etching reaction of ferric chloride with nickel is thermodynamically quite favorable, the kinetics of the reaction are intolerably slow. Agitation of the solution during etching increases the reaction rate somewhat, but not significantly. The same situation is true in etching other metals such as molybdenum and other alloys that include iron and nickel. Such alloys include Kovar, composed of 29% nickel, 17% cobalt and 53% iron. Kovar is manufactured and sold by Westinghouse Electric Corporation and is known for its thermal expansion characteristics that match hard glass. Another alloy that is difficult to etch is sold under the trademark INVAR and is formed of a mixture of iron and nickel. INVAR has a low coefficient of thermal expansion. Another alloy is sold under the trademark INCONEL composed of a combination of nickel and chromium. INCONEL is manufactured and sold by International Nickel Company and is corrosion resistant. Other alloys that are difficult to etch include brass, which is a combination of copper and zinc; bronze, which is a combination of copper and tin; steel, which is an alloy of iron and from 0.02 to 1.5% carbon; and stainless steel, which is composed of steel with an additive, usually chromium or nickel. The etching of molybdenum is particularly important in the production of masks used in the electronic industry. The etchant solutions used in the practice of our invention depends upon the oxidation of the metal being etched to an ion that is soluble in the etching solution. The etching process involves an oxidation-reduction reaction by an active ingredient in the etchant bath that oxidizes the metal to produce a metal ion which goes into the solution. For example, when etching nickel the following reaction occurs:



The etching solutions contemplated for use in the practice of this invention include ferric ions, ferricyanide ions, ceric ions, dichromate, chromate, and iodine. Typically, ferric ions are provided in a ferric chloride solution with a pH in the range of -1 to 3. Ferricyanide ions are provided in a potassium ferricyanide solution with a pH in the range of 9 to 14, and ceric ions are provided in a ceric ammonium nitrate solution with a pH in the range of -1 to +2. Iodine is provided in a KI-I<sub>2</sub> solution. Such solutions are commonly used to strip gold and nickel.

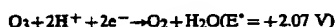
Obviously other cations or anions can replace the nonreactive cations or anions in the above solutions. For example, ferric bromide or ferric nitrate can be used instead of ferric chloride. The etchant solutions can have any suitable concentration of active ingredients that will satisfactorily etch the chosen metal.

It has been discovered that the addition of ozone to the etching solution when etching the aforementioned

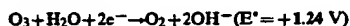


metals materially increases the etching rate and also rejuvenates the active oxidizing ingredient in the solution. Generally, the etching rate is increased significantly more than solution agitation alone would achieve, as will be proven in the examples that follow. In addition, the rejuvenation of the solution is simultaneously achieved without the addition or formation of agents in the solution that would otherwise hamper the etching reaction and/or reduce the effective life of the solution. The addition of ozone to an etching bath is straightforward, simple in operation, and scalable to large or small operations. The ozone addition leaves no chemical residue in the solution or on the equipment or backing layers. Further, the etch rate enhancement can be controlled by controlling the amount of ozone added to the etching solution.

The redox chemistry of ozone in acid solution is described by the half reaction:

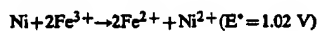


and in base solution

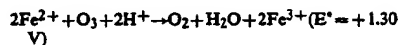


Next to fluorine and its oxides, ozone is the most powerful oxidant. It will thus reverse any redox reaction of  $E^* < 2.07 \text{ V}$  in acid and  $E^* < 1.24 \text{ V}$  in base. Any etchant which involves a redox couple of a potential within these ranges is thus amenable to ozone reoxidation.

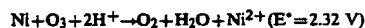
The recycling sequence for ferric ions is thus



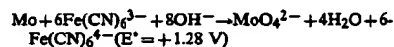
and



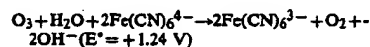
which combine to:



For ferricyanide the rejuvenation reactions are as follows:



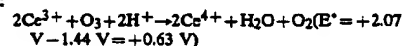
and



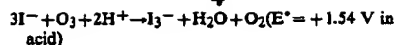
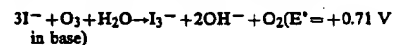
which combine to:



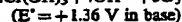
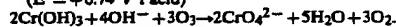
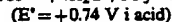
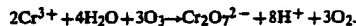
Cerium redox chemistry is reversible as per the reaction:



Iodine/iodide reoxidation is as follows:



Chromium reoxidation for rejuvenation of etching is as follows:



Ozone can be produced very easily by commercially available generators. The ozone is generated by passing oxygen through a silent corona discharge. From there the  $\text{O}_2\text{-O}_3$  stream is piped directly to the etchant bath where it is preferably passed through a glass frit filter and into the bath to produce bubbles. The product gas can be exhausted up through exhaust vents. The vigor of the bubbling should not be so great as to spatter the solution. A typical gas delivery is 5 cu. ft./hr. of 5 psi gas through 3 liters of 75% w/w ferric chloride. The gas introduced into the etching solution will vary somewhat but is preferably in the range of from 0.1 to 10% ozone, more preferably in the range of 2% to 9% by weight ozone, with the balance being  $\text{O}_2$ . The increase in etching rate of metal achieved by the addition of ozone, compared to etching by conventional techniques, will vary somewhat depending on the metal being etched and the specific etching solution. However, the increase in etching rate is significant and varies from 4 to 20 times the etching rate compared to processes where no ozone is used.

The following examples are presented to illustrate preferred embodiments of the process of our invention, and should not be construed to unduly limit the scope of the claims.

#### EXAMPLE 1

Metal etch specimens were prepared by placing a release layer of polymethyl methacrylate on a backing sheet, laminating a 1 mil thick nickel foil onto the release layer, placing a photoresist layer over the metal, and exposing and developing the resist layer exposed to form a pattern on the layer. The areas of the photoresist were removed. The resulting specimen was immersed in a 75% w/w ferric chloride solution at a temperature of 20° C., and the etching action observed. When the uncovered nickel areas were removed by etching, the specimen was removed from the etchant bath that the etching time noted. The total time of immersion, necessary to etch through the 1 mil thick nickel layer, was 6 hours.

#### EXAMPLE 2

An unetched specimen as prepared in Example 1, was immersed in the same ferric chloride solution at the same temperature, and 9% by weight ozone in  $\text{O}_2$  was bubbled through the solution at a rate of 5 ft.<sup>3</sup>/hr. at an overpressure of 5 psi. The specimen was removed when the exposed portion of the nickel foil was etched away. The total time of immersion necessary to etch the exposed nickel foil was found to be 53 minutes. This represents a 6.8 fold increase in the etchant rate compared to the process of Example 1. It was also noted that neither the photoresist nor the backing layer was affected by the etching action. This demonstrates a dramatic increase in the etching rate of Ni by ferric chloride achieved by the process of the invention.

## EXAMPLE 3

In order to determine what effect the agitation of the solution by itself has on etching rate, a specimen, as prepared in Example 1 was immersed in the same ferric chloride solution at the same temperature in the same tank, and oxygen bubbled through the etchant at a rate of 5 ft.<sup>3</sup>/hr. at 5 psi. After 32 minutes the specimen was removed, the thickness of the exposed nickel film measured, and the average etchant rate calculated. It was observed that the oxygen agitation produced only a 2.5 fold increase in the etchant rate as compared to Example 1.

## EXAMPLE 4

The same procedure described in Example 3 was followed except that nitrogen was bubbled through the etching solution at a rate of 5 ft.<sup>3</sup>/hr at 5 psi. The total time to etch through the nickel layer was calculated and compared to the time and etch rate of Example 1. It was found that nitrogen agitation also produced a 2.5 fold increase in the etchant rate as compared to Example 1. Examples 3 and 4 indicate that the etchant rate can be increased by agitation of the solution, but the increase in rate is materially less than the rate increase achieved by the process of the invention. The similar etch rates using O<sub>2</sub> and N<sub>2</sub> indicate that the increase is due solely to agitation.

## EXAMPLE 5

As a control, a strip of shiny molybdenum metal weighing 3.3510 g was immersed in a spent etchant bath approximately one month old having roughly 22-24% by weight of potassium ferrocyanide plus potassium ferricyanide, plus 1.3% to 2.6% molybdenum (dissolved as molybdate, MoO<sub>4</sub><sup>2-</sup>), with a pH of 12.5, for 30 minutes. The strip was removed and weighed. The weight was 3.1839 g, which represents a 5.0% weight loss.

## EXAMPLE 6

The procedure of Example 5 was repeated using molybdenum strips with the same surface area and thickness as the strips used in Example 3, except that oxygen gas was bubbled through the etchant while the molybdenum strip was immersed. The strip underwent a 9.7% weight loss. The increase in the etchant rate was attributed to agitation of the etchant.

## EXAMPLE 7

The spent etchant bath of Example 5 was ozonated with a 9% O<sub>3</sub> in oxygen for 1 hour, and subsequently a strip of molybdenum was weighed and immersed as the bubbling of O<sub>3</sub> in oxygen was continued. The molybdenum strip had the same surface area, and thickness as the strips used in Examples 5 and 6. After 40 minutes the strip was removed and weighed. It was found to have undergone a 34.7% weight loss. A second strip was subsequently weighed and immersed for 1 hour as ozone in oxygen was bubbled through the etchant. After an hour the strip was removed and weighed. It had undergone a weight loss of 38.3%. The experiment proves that spent solutions of potassium ferricyanide can be rejuvenated by ozone, that the etchant rates in such solutions are reproducible, and are significantly higher than when no agitation, or when agitation of the solution is provided.

## EXAMPLE 8

An etch bath consisting of 2 liters of K<sub>3</sub>Fe(CN)<sub>6</sub> (146 gm/liter) with some dissolved molybdenum (9 g Mo/-liter), a pH of 11.5, and a temperature of 46° C. was ozonated as previously described. A Mo sheet with a resist layer thereon defining a pattern was immersed in the bath. After two hours of etching the etchant penetrated through the Mo sheet. After 3 hours of etching the resist layer sheeted off as a brown film. This performance is contrasted with the normal spray etching of the Mo sheet where the etchant is at 60° C., and a pH of 12.5. Even with 30-40 minutes of exposure to the etchant, the resist barely survives. Survival of the resist for 3 hours of etching is unheard of, as is operation at a pH as low as 11.5. The example points up the advantages of the process of the invention i.e., (1) a lower pH permits longer resist life, (2) a lower temperature diminishes vapor loss from the bath and (3) the increased rate of etching improves throughput.

## EXAMPLE 9

A depleted aqueous molybdenum etching solution chosen to be regenerated contained originally 215 grams/liter K<sub>3</sub>Fe(CN)<sub>6</sub>, plus 71.6 grams/liter KOH to raise the pH to 13.75. The virgin etchant before depletion has a potential of +0.462 mV. After repeated uses as a molybdenum metal etchant the bath is normally dumped at some arbitrary potential of the order of 0.380 mV.

One liter of this golden solution was ozonated (by the process of the invention) at 5 scf/hr, of 8-9% O<sub>3</sub> in O<sub>2</sub>, for 15 minutes. This turned the solution back to a dark cherry red color. No ozone odor could be detected emanating from the solution during the ozonolysis. The O<sub>3</sub> odor was evident only at the end of this period, at which point the ozonolysis was terminated.

The potential of the golden solution was initially measured and found to be +0.398 mV before ozonolysis. The cherry red solution obtained after ozonolysis had a potential of +0.462 mV, indicating that the re-conversion of the Fe(CN)<sub>6</sub><sup>4-</sup> back to Fe(CN)<sub>6</sub><sup>3-</sup> by the process of the invention was successful.

## EXAMPLE 10

A KI-I<sub>2</sub> bath, used for stripping gold and nickel was investigated which consisted of the following:

Species	Concentration	Moles/l
KI	479 gm/liter	2.885
I <sub>2</sub>	118 gm/liter	0.464

The iodine bath solution was depleted by use to the point where it would ordinarily be dumped. A 200 ml aliquot of the depleted KI-I<sub>2</sub> was withdrawn from the bath and assayed at 60.3 gm/liter (51% of the original concentration) of I<sub>2</sub> by a thiosulfate titration. The aliquot of bath was then ozonated at full power, i.e., 9% O<sub>3</sub> in O<sub>2</sub> for 10 minutes at 5 ft.<sup>3</sup>/hr. After 10 minutes, examination revealed that the dispersion tube for introducing O<sub>3</sub> was coated with I<sub>2</sub> crystals. After one hour of further ozonolysis the solution was again assayed to determine iodine concentration. The thiosulfate titration determined the iodine concentration to be approximately 130 gm/liter, which concentration exceeded the original concentration of the first assay by more than 10%.

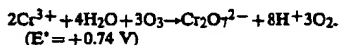
## EXAMPLE 11

49.17 grams of  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  was dissolved in 100 ml of water. The solution contained 89.7 mmoles of  $\text{Ce}^{4+}$ , which is theoretically sufficient to etch 1.554 grams of chromium. 15.37 grams of chromium granules, averaging 1 mm in diameter, were added to the solution as oxygen was bubbled through it for agitation. In 15 minutes the granules of chromium were removed and weighed. The original 15.37 grams of granules were reduced to 15.10 grams, a loss of 0.27 grams. The chromium granules were reintroduced into the solution and left there for 5 days, during which time an additional 0.79 grams of chromium dissolved in the ceric ammonium nitrate solution. Subsequently, the etchant solution was decanted from the chromium granules and a 9%  $\text{O}_3$  in  $\text{O}_2$  stream bubbled through the solution at a rate of 5 ft.<sup>3</sup>/hr for three hours to regenerate it. During this time the solution turned from green to orange-red. A potentiometric titration indicated the presence of  $\text{Cr}_2\text{O}_7^{2-}$  as well as  $\text{Ce}^{4+}$  ions.

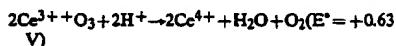
The chromium granules were replaced in the etching solution. In only 15 minutes 15.53 grams of chromium were reduced in weight to 15.16 grams, a loss of 0.37 grams. The  $\text{O}_3$  regenerated solution thus etched chromium at a rate of 37% faster than the initial fresh solution. The chromium (III) product was oxidized by the  $\text{O}_3$  to the chromium (VI) species, i.e.,  $\text{Cr}_2\text{O}_7^{2-}$ , as evidenced by the color change of the solution to red.

The example indicates that  $\text{O}_3$  will recycle the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  redox couple. When the solution is used to etch chromium metal,  $\text{Cr}^{3+}$  ions are released into the solution. The  $\text{O}_3$  bubbled through the solution oxidizes the  $\text{Cr}^{3+}$  ions to  $\text{Cr}_2\text{O}_7^{2-}$ . This was clearly evident not only from the potentiometric titration, but also from the deepening red color of the solution as more and more Cr is etched and the Cr ions were reoxidized to  $\text{Cr}_2\text{O}_7^{2-}$  which is a reddish color.

When the  $\text{Ce}^{4+}$  solution is used to etch chromium, both of the products of the reaction, i.e.  $\text{Cr}^{3+}$  and  $\text{Ce}^{3+}$ , are susceptible to ozone reoxidation i.e.,



and



The chromium reoxidation will precede the cerium reoxidation because of the higher emf value. When an excess of chromium is present in the solution the  $\text{Ce}^{4+}$  ions will be depleted, and the rate of etching will drop to nearly zero since the rate is proportional to  $[\text{Ce}^{4+}]$ . Any  $\text{Ce}^{3+}$  converted back to  $\text{Ce}^{4+}$  by ozone will immediately be consumed by etching the excess chromium metal present. The recycling was evident when the chromium was filtered from the etchant solution.  $\text{O}_3$  was then used to regenerate  $\text{Ce}^{4+}$  in sufficient concentration so that when chromium metal was reintroduced into the etchant an enhanced etch rate was observed.

This Example also illustrates that chromium (III)-Chromium (VI) etching systems can be recycled.  $\text{H}_2\text{Cr}_2\text{O}_7$  in  $\text{H}_2\text{SO}_4$  is used to etch copper, iron-cobalt-vanadium alloys, Kovar, nickel-silver alloys, phosphor-bronze, and silver. In general ozone will recycle any

candidate species, including products of an etching, to the highest state achievable.

While the present invention has been particularly shown and described with reference to preferred embodiments therefor, it will be understood by those skilled in the art that the foregoing and other changes in form and detail may be made therein without departing from the spirit and the scope of the present invention, as defined in the appended claims.

We claim:

1. An etching process in which a metal is dissolved as cations from a surface of a body by contact with an etching solution comprising,

contacting said metal, selected from the group consisting of Ni, Sn, Cu, Cr, and alloys of steel, stainless steel, with an etching solution, said etching solution having an active etching ingredient selected from the group consisting of ferric ions, ferricyanide ions, chromate ions, and dichromate ions,

simultaneously introducing ozone into said etching solution to rejuvenate said solution, and to materially increase the etching rate of the metal.

2. The etching process of claim 1 wherein said etching solution includes ferricyanide anions.

3. The etching process of claim 1 wherein said metal is Ni, and said etching solution has ferric ions as an active ingredient, and chloride anions, said solution having a pH in the range of -1 to +3.

4. The etching process of claim 1 wherein said ozone is formed by passing oxygen through a silent corona discharge.

5. The etching process of claim 4 wherein said ozone is bubbled through said etching solution.

6. The etching process of claim 1 wherein said body is comprised of a flexible backing element of an organic dielectric material that supports a layer of said metal.

7. The etching process of claim 6 wherein said body is prepared for selectively etching areas of said metal by depositing, exposing, and developing a resist layer on said metal that blankets selected areas of the metal and prevents contact of said etching solution.

8. The etching process of claim 1 wherein said ozone is introduced into said etching solution in a stream of oxygen and wherein the percent of ozone by weight is in the range of 0.1% to 10%.

9. The etching process of claim 1 wherein Mo is dissolved as anions from a surface of a body by contact with an etching solution, wherein said solution is a basic ferricyanide aqueous solution,

simultaneously introducing ozone into said etching solution to rejuvenate said solution, and to significantly increase the etching rate of said solution.

10. The etching process of claim 4 wherein said etching solution is an aqueous solution and further includes potassium or sodium cations.

11. The etching process of claim 10 wherein said etching solution has a pH in the range of 9 to 14.

12. The etching process of claim 11 wherein said body is prepared for selectively etching areas of said metal by depositing, exposing, and developing a layer of resist on said metal that blankets selected areas of the metal and prevents contact of said etching solution.

13. The etching process of claim 12 wherein said ozone is formed by passing oxygen through a silent corona discharge.

14. An etching process in which a metal is dissolved as cations from a surface of a body by contact with an

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etching solution containing an active oxidizing agent comprising,

contacting molybdenum with a solution containing an active agent consisting of a reduction-oxidation couple to be reversed with an electromotive force of less than 2.07 V in an acid solution, and an oxidation-reduction couple to be reversed with an

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electromotive force of less than 1.24 V in basic solution, introducing ozone into said etching solution to rejuvenate said solution and increase the etching rate.

15. The etching process of claim 14 wherein said etching solution contains ferricyanide ions.

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**United States Patent** [19]  
**David**

[11] **Patent Number:** **4,995,942**  
[45] **Date of Patent:** **Feb. 26, 1991**

[54] **EFFECTIVE NEAR NEUTRAL PH ETCHING SOLUTION FOR MOLYBDENUM OR TUNGSTEN**

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[73] **Assignee:** **International Business Machines Corporation, Armonk, N.Y.**

[21] **Appl. No.:** **516,845**

[22] **Filed:** **Apr. 30, 1990**

[51] **Int. Cl.<sup>3</sup>** ..... **B44C 1/22; C23F 1/00; C09K 13/00**

[52] **U.S. Cl.** ..... **156/642; 156/656; 156/664; 252/79.1; 252/79.2; 252/79.5**

[58] **Field of Search** ..... **252/79.1, 79.2, 79.4, 252/79.05; 156/642, 656, 659.1, 664; 437/228, 245; 134/3, 10, 41**

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*Primary Examiner*—William A. Powell  
*Attorney, Agent, or Firm*—Ira David Blecker

[57] **ABSTRACT**

A neutral or near neutral pH etching solution for effectively etching molybdenum and tungsten including: an aqueous ferricyanide ion solution, a soluble molybdate or tungstate, and an essential compound such that upon combination of said soluble molybdate or tungstate and said essential compound, a heteropoly compound is formed in which said essential compound contributes at least one heteroatom to said heteropoly compound.

The etching solution is most preferably used for etching molybdenum or tungsten which is adhered or proximate to a base-sensitive material.

**21 Claims, No Drawings**

## EFFECTIVE NEAR NEUTRAL PH ETCHING SOLUTION FOR MOLYBDENUM OR TUNGSTEN

### FIELD OF THE INVENTION

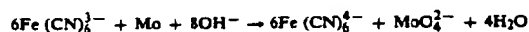
This invention relates to the field of etching solutions for refractory metals such as molybdenum and tungsten. More particularly, this invention relates to those etching solutions which can effectively etch molybdenum and tungsten at nearly neutral pH.

### BACKGROUND OF THE INVENTION

Various etchants are well known for etching molybdenum and tungsten. For example, molybdenum may be easily etched in ferricyanide solutions as disclosed in Acocella et al., U.S. Pat. No. 4,747,907, the disclosure of which is incorporated by reference herein. Similarly, tungsten may be etched by a mixture of hydrogen peroxide and aqueous ammonia. This tungsten etchant, however, has a shelf life of only about 8 hours. Tungsten etches very slowly, if at all, in ferricyanide solutions.

For many purposes, the performances of these etchants are acceptable. These etchants, however, are not satisfactory in some applications.

To illustrate this, the etching of molybdenum is typically effected in a strongly alkaline solution of ferricyanide:



The pH of such an etchant solution is typically maintained between about 12.0 and 13.0 and temperature at about 50–55 degrees Centigrade.

David and Kurdziel, "Ozone Reoxidation of a Ferricyanide Bath for Etching Molybdenum," *Metal Finishing*, p. 47–49 (May 1988), have deduced the rate law for ferricyanide etching of molybdenum. It was concluded that by enhancing a ferricyanide solution with molybdate and by buffering the solution to control pH, good etching results may be obtained. It was necessary to maintain the pH at a relatively high level, 12.0 to 12.5.

One such application where this etchant would be unsatisfactory is when the molybdenum, for example, is incorporated in a laminate structure which is comprised of the metal and a base-sensitive low dielectric constant polymer such as a polyimide. These types of polymers will hydrolyze in strong bases and thus cannot survive current methods of etching molybdenum.

It would thus be desirable to have an etchant for molybdenum, and tungsten as well, which has a lower pH that will not adversely affect base-sensitive materials.

Lowering the pH of a molybdenum etchant, however, is not a trivial process. If the pH of a ferricyanide etch bath drops below about 10–11, the molybdenum blackens due to the formation of polymolybdates as follows:



This stops the etching process completely.

Thus, a low pH etching process for molybdenum must preserve the etching rate and suppress the formation of undesirable molybdate polymer residues, as well

as not hydrolyze companion polymers in the laminate or composite structure.

It has been discovered, however, that the pH may in fact be lowered in a molybdenum etchant solution without slowing down the etching rate and while suppressing the formation of undesirable molybdate polymer residues. It has also been discovered that the pH may be lowered for a tungsten etchant solution as well. The key is in the formation of heteropoly compounds, a class of compounds known in the literature for many years. See, for example, Tsigdinos, "Heteropoly Compounds of Tungsten and Molybdenum" in *Topics In Current Chemistry*, 76 (Springer-Verlag, 1978), the disclosure of which is incorporated by reference herein.

Accordingly, it is a prime object of the present invention to have a near neutral pH etching solution for effectively etching molybdenum and tungsten.

It is a further object of the invention to have a near neutral pH etching solution that is capable of being recycled.

### BRIEF SUMMARY OF THE INVENTION

The objects of the invention have been achieved by providing, according to one aspect of the invention, a neutral or near neutral pH etching solution for effectively etching molybdenum and tungsten comprising: an aqueous ferricyanide ion solution, a soluble molybdate or tungstate and an essential compound such that upon combination of said soluble molybdate or tungstate and said essential compound, a heteropoly compound is formed in which said essential ingredient contributes a heteroatom or heteroatoms to said heteropoly compound.

According to another aspect of the invention, there is provided a method of effectively etching molybdenum or tungsten from a composite material comprising molybdenum or tungsten adhered to a base-sensitive material without damaging the material comprising the steps of: contacting the composite with a neutral or near neutral pH etching solution comprising: an aqueous ferricyanide ion solution, a soluble molybdate or tungstate, and an essential compound such that upon combination of said soluble molybdate or tungstate and said essential compound, a heteropoly compound is formed in which said essential compound contributes a heteroatom or heteroatoms to said heteropoly compound.

### DETAILED DESCRIPTION OF THE INVENTION

The key to the present invention is to form heteropolymolybdates and heteropolytungstates as part of the etching process of molybdenum and tungsten, respectively. Generally, heteropoly compounds have been known for years. The novel aspect of the present invention is to apply these heteropoly compounds to the current needs of improving the etching of molybdenum and tungsten.

The heteropoly compounds generally consist of two to eighteen hexavalent molybdenum or tungsten atoms surrounding one or more central atoms (heteroatoms). Often vanadium, niobium, tantalum, or other transition metals can replace some of the molybdenum or tungsten atoms in the heteropoly structure.

In the case of molybdenum etching with a ferricyanide solution, the heteropoly compound may be formed by combining in solution a soluble molybdate and an essential compound that contributes at least one heteroatom to the formed heteropolymolybdate. A preferred

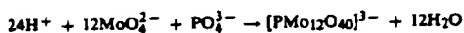
soluble molybdate is sodium molybdate and a preferred essential compound, for purposes of the present invention, is phosphoric acid. As will become apparent hereafter, there are a number of essential compounds that may be utilized. The appropriate one chosen will often depend on the intended application.

It should be understood that some of the soluble molybdate



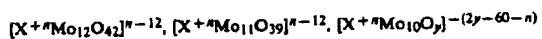
necessarily comes from the etching and dissolution of the molybdenum. The bulk of the soluble molybdate, however, preferably (and usually) comes from the addition to the etching solution of soluble molybdates such as sodium molybdate.

One example of the formation of heteropolymolybdates is the following reaction:



where phosphorus is the heteroatom contributed by the phosphoric acid, the essential compound. The fact that the phosphoric acid is an essential compound will become apparent hereafter. This reaction may take place at room temperature as well as at elevated temperatures.

There are literally hundreds of these heteropolymolybdates: The heteroatom may alternatively be, for example, silicon, germanium, sulfur, aluminum, nickel, manganese, arsenic, titanium, zirconium, etc. Those heteropolymolybdates which include phosphorus are among the most easily synthesized and so are preferred. Some examples of other heteropolymolybdates are



where X + n can be  $\text{Si}^{+4}$ ,  $\text{Ge}^{+4}$ ,  $\text{Al}^{+3}$ ,  $\text{Ni}^{+4}$ , etc.

As an example, the above reaction may proceed with sulfurous acid instead of phosphoric acid, in which case the heteroatom will be sulfur. The heteropolymolybdate has the general formula  $[\text{SMo}_x\text{O}_y]^{6(x+1)-2y}$ , and one specific heteropolymolybdate is  $[\text{SMo}_{12}\text{O}_{40}]^{2-}$ . The ease of using common liquid-phase acids as sources of heteroatoms favors the usage of phosphoric acid and sulfurous acid. Phosphoric acid, which emits no volatile gas, is easier to handle than sulfurous acid, which emits sulfur dioxide, and so is preferred over sulfurous acid.

It bears emphasis that the heteroatom source (i.e., the essential compound) need not be an acid. For example, one could add phosphate as sodium phosphate, sulfite as sodium sulfite, or arsenic as sodium arsenate. The acids (e.g., phosphoric or sulfurous acid) are convenient liquids to use, but other heteroatom sources will also suffice.

These polyions are amazingly soluble; their salts can be dissolved in only a fraction of their weight in water. This fulfills a basic condition of etching any metal, to wit, the etched product must remain soluble.

Conventional etching of molybdenum in ferricyanide solutions normally requires a high pH of about 12 to 12.5, and perhaps as high as 13 to maintain the soluble molybdenum species as



Also, etching typically takes place at elevated temperatures, about 55 degrees Centigrade. With the present invention, molybdenum is maintained as a soluble polymolybdate at nearly neutral pH and etching may proceed at room temperature. Of course, etching according to the present invention may also proceed at elevated temperatures if higher etch rates are desired.

As will be appreciated by those skilled in the art, it usually be necessary to introduce a charge balancing species into the reaction. The choice of charge balancing species is not critical although the introduction of undesirable stray ions such as chlorine should be avoided if possible. Preferred charge balancing species include sodium, potassium, and ammonium ions, which may be added by their hydroxides, phosphates, or molybdates. Of course, this list of charge balancing species is not exhaustive and may include other charge balancing species as well.

In view of the presence of analogous tungsten heteropolyions, it was theorized by the present inventor that similar efficacious results could be obtained in the etching of tungsten. When a solution of ferricyanide, sodium tungstate, and phosphoric acid was formulated and used to etch tungsten, favorable results similar to those obtained in the etching of molybdenum were obtained at nearly neutral pH. Interestingly, a ferricyanide solution alone would not etch tungsten to any practical degree.

An important application of the present invention is to etch molybdenum or tungsten from a laminate comprising molybdenum or tungsten and base-sensitive materials such as polyimide polymers. The molybdenum or tungsten may be adhered directly to the base sensitive materials or may be merely proximate to the base sensitive materials. The laminate may also comprise additional metals such as copper. It was found that the molybdenum or tungsten may be etched from polyimide, for example, without causing any degradation of the polyimide material or additional metal since the optimal pH range for the etchants according to the invention is about 6 to 8.

Further advantages of the present invention will become more apparent after referring to the following examples.

## EXAMPLES

In the following examples, all reagents were used as received from the vendor with no further purification. Potassium ferricyanide was obtained from Duso Chemical Co. (Poughkeepsie, N.Y.). Sodium tungstate dihydrate, sodium molybdate dihydrate, sodium borate (Borax), sodium hydroxide, and potassium hydroxide were obtained from Mallinckrodt, Inc. Phosphoric acid was obtained from Ashland Chemical and sulfurous acid was obtained from Fisher Scientific. Deionized water was used in all etching solutions.

### EXAMPLE 1

73 grams of potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) and 60 grams of sodium molybdate dihydrate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ) were dissolved in 500 milliliters of deionized water. The pH of the solution was 8.55. A sheet of molybdenum metal weighing 1.6705 grams was immersed in this stirred etchant at room temperature (20 degrees Centigrade). In 28 minutes, the pH had dropped to 6.98 and the molybdenum was coated with a black layer which could not be rinsed away. After etching, the molybdenum sheet weighed 1.6557 grams, a net loss of 14.8 milligrams.

## EXAMPLE 2

73 grams of potassium ferricyanide and 60 grams of sodium molybdate dihydrate were dissolved in 500 milliliters of deionized water. 3 milliliters of phosphoric acid ( $H_3PO_4$ ) were added, followed by addition of sufficient quantities of potassium hydroxide (KOH) pellets (about 5 grams) to raise the pH to 7.57. A molybdenum sheet weighing 1.5483 grams was suspended in this solution at room temperature. In 30 minutes, the molybdenum sheet weighed 1.5112 grams for a net loss of 37.1 milligrams. The molybdenum had an orange coloration but this rinsed off easily with water to leave a shiny surface.

## EXAMPLE 3

The phenomenon of Example 2 is not due to pH alone as this example will illustrate. 73 grams of potassium ferricyanide, 60 grams of sodium molybdate dihydrate and 5 grams of borax (sodium borate) were dissolved in 500 milliliters of water. The pH of the solution was 9.52. A molybdenum sheet weighing 2.2579 grams was immersed in this etchant. After 27 minutes, the pH had dropped to 7.0 and the molybdenum sheet had blackened. Addition of potassium hydroxide pellets raised the pH to 9.42 but did not dissolve the black coating nor did it render the coating rinsable. Immersion of the molybdenum sheet in the etchant for another 20 minutes caused the pH to drop to 9.3. Next, 5.1 more grams of borax was added. The sheet was immersed for 25 more minutes, in which time the pH dropped further to 8.7. The mass of the sheet was 2.2436 grams after a total of 72 minutes of etching, a loss of only 14.3 milligrams.

## EXAMPLE 4

To the solution in Example 3, 3 grams of potassium hydroxide and 3 milliliters of phosphoric acid were added, which adjusted the pH to 7.85. This restored the etching potency of the solution. When the blackened molybdenum sheet was again immersed in the solution, the molybdenum sheet became shiny again. After 3 hours of immersion in this etchant, the molybdenum sheet became a mass of shredded debris. This example clearly indicates the unique role that the phosphoric acid plays in the etching of molybdenum.

The phosphate from the phosphoric acid reacted with the insoluble black molybdenum oxides on the surface of the molybdenum sheet, forming heteropolymolybdates and allowing the etching to proceed. It is the formation of these phosphomolybdate polyions which accounts for the etching performance observed. Under the above conditions, the borax did not incorporate any heteroatoms into a molybdate polyion, and thus did not effect any etching.

## EXAMPLE 5

A solution of 60 grams of sodium molybdate dihydrate and 3 milliliters of phosphoric acid in 500 milliliters of deionized water was adjusted to pH 7.31 by the addition of potassium hydroxide pellets. No weight loss was observed after 54 minutes of immersion of a sheet of molybdenum, a control experiment which indicated that the combination of phosphoric acid (phosphate) with molybdate did not etch molybdenum.

## EXAMPLE 6

To the solution of Example 5, 73 grams of potassium ferricyanide was added, wherein the pH rose to 7.73. A

36.5 micron thick sheet of molybdenum laminated to a 14 micron thick cured, low-TCE polyimide sheet was placed in the stirred etchant. After 30 minutes, the pH had dropped to 7.65. After 17.5 hours, the pH had dropped to 7.59. No evidence of any precipitate was visible in the etchant. The polyimide film had survived intact and had retained its original clear yellow color, but the molybdenum was gone. The polyimide film exhibited no degradation even after 42 hours of continuous immersion in the etchant.

## EXAMPLE 7

A polyimide/molybdenum composite with copper pads patterned between the polyimide layer and the molybdenum, similar to the composite in Example 6, was etched in a solution similar to Example 6. The composite was etched for 16 hours at room temperature at pH ranging from 7.77 at the beginning of the etching trial to 7.66 at the end. This removed the molybdenum from the composite, except for a few scattered bits of tenacious molybdenum metal. None of the copper pads had delaminated from the polyimide and the polyimide film exhibited no degradation from the etching process.

## EXAMPLE 8

The etchant from Example 7 was used to etch 4.4693 grams of molybdenum sheets. After 11.75 hours, the etchant pH had fallen to 6.6 from 7.59 and a precipitate sludge had formed at the bottom of the beaker. Enough potassium hydroxide pellets were added to raise the pH back up to 7.61, which also dissolved the precipitate and which turned the solution a dark orange color. After 24.5 more hours of etching, 0.2034 grams of molybdenum had survived. The etchant was then treated with ozone (5 scf/hr, 5 psi overpressure; GL-1 Ozone Generator from PCI, West Caldwell, N.J.) for 25 minutes, which restored the potential to +460 millivolts and raised the pH back up to 12.95. This red etchant was titrated with phosphoric acid back to pH 7.78. The etchant has thus been recycled.

A molybdenum sheet weighing 2.2007 grams was etched for nine minutes in the regenerated etchant. During this time, the pH remained constant between 7.77 and 7.78, and the weight of the sheet decreased 25.2 milligrams.

The pH is occasionally adjusted during or after each ozone recycle with potassium hydroxide (or sodium hydroxide) pellets and/or phosphoric acid, or alkali metal phosphates. The addition of the acid (phosphate) is also necessary to form heteropolymolybdates from the newly dissolved molybdenum from prior etching runs.

## EXAMPLE 9

Further evidence for the heteropolymolybdate mechanism is the versatility of formation of pH-neutral etchants with other heteroatom sources. Sulfurous acid can be used instead of phosphoric acid in this etchant system, which yields a solution of similar pH and performance.

73 grams of potassium ferricyanide and 66.17 grams of sodium molybdate dihydrate were dissolved in 500 milliliters of water, yielding a solution of pH 10.52. 0.8 milliliters of sulfurous acid ( $H_2SO_3$ ) was added, which lowered the pH to 7.5. A strip of molybdenum metal weighing 2.1753 grams was immersed in the solution. After only six minutes, the pH had dropped to 7.28. Addition of 3.3 milliliters of sulfurous acid and 3 potas-



sium hydroxide pellets (about one gram) raised pH back to 7.42. After 15 minutes of etching, the molybdenum strip was rinsed clean in an ultrasonic bath and weighed. The weight loss, 0.2599 grams, was 11.9% of the original strip.

The molybdenum was returned to the etchant. After one hour, the pH had dropped to 6.99 and the strip had acquired a black coating which could not be rinsed off. Four grams of potassium hydroxide pellets were added to the solution, which raised the pH to 7.16. The black layer could then be easily washed off in an ultrasonic bath of this etchant. The strip weighed 1.1188 grams, a 48.6% weight loss in one hour.

While the use of sulfurous acid to incorporate sulfur into the heteropolymolybdate has been demonstrated, the incorporation of other heteroatoms, such as arsenic, aluminum, silicon, etc., should also be feasible.

#### EXAMPLE 10

74.1 grams of potassium ferricyanide was dissolved in 500 milliliters of water, yielding an orange solution of pH 9.88. This solution failed to etch a strip of tungsten weighing 2.9338 grams in 30 minutes. 100.1 grams of sodium tungstate dihydrate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ) was then added, raising the pH to 10.25. After 30 minutes, the pH had dropped to 9.8 and the weight of the tungsten had decreased to 2.7358 grams for a net loss of 0.198 grams. While this etchant is satisfactory for some purposes the pH is still too high for base-sensitive materials.

Addition of 3 milliliters of phosphoric acid caused the immediate formation of a yellow precipitate in the etchant, and a small pH drop to 9.62. Addition of enough sodium hydroxide pellets to raise the pH to 13.38 did not dissolve this precipitate. More precipitate, this time chrome-yellow, formed on further addition of enough phosphoric acid to lower the pH to 3.2. When pH was raised to 4.67 with more sodium hydroxide pellets, some of the precipitate dissolved and the suspension turned mustard yellow. Addition of more sodium hydroxide raised the pH to 5.0 and cleared the suspension even more, turning the solution olive green, with some green residue still floating around in the etchant.

Over the next 3 days, the tungsten lost very little weight (less than 5 milligrams) at an etchant pH of less than or equal to 5.5. When the pH was raised to 5.95, weight loss recommenced; the tungsten strip lost 0.3079 grams in 75 minutes. Steady addition of sodium hydroxide pellets over the next 85 minutes raised pH up to 6.34, during which time the weight of the strip decreased another 0.1503 grams. Addition of sodium hydroxide pellets was continued, producing a steady increase in etch rate as the pH was raised, eventually ending at 7.0.

This etchant operated best in the range of about pH 6 to 8, yielding similar etch rates to those observed with the molybdenum etchant. As demonstrated, a ferricyanide solution alone would not etch tungsten. The addition of sodium tungstate was necessary in order to commence the etching reaction, which indicates that the tungstate ions play a similar, but even more decisive role in the ferricyanide etching of tungsten than molybdate does in molybdenum etching. The phosphotungstate etchant is best made by first adding base to the tungstate-ferricyanide solution, the adding acid to avoid premature precipitation of a tungsten oxide colloid (as demonstrated earlier in this example) if the pH drops well below pH 7. The phosphate can also be added as its alkali metal derivative.

This etchant is also advantageous over the prior art etchant of hydrogen peroxide and ammonia in that the etchant according to the present invention has an indefinite shelf life whereas the prior art etchant is only stable for about 8 hours.

#### EXAMPLE 11

The etchant from Example 10 was used to etch tungsten until about 95% of the ferricyanide had been consumed and the etch rate became negligible. The exhausted etchant was then treated with ozone for 40 minutes, during which time the pH rose from 7.02 to 8.08, the solution color changed from yellow to red, and a precipitate settled to the bottom of the beaker. This precipitate was filtered off to yield a clear red rejuvenated etchant, ready for further etching of tungsten.

One advantage of the present invention which is perhaps not readily apparent is that if one would want to adjust the pH of the etching solution below 12 to 13, but above nearly neutral 6 to 8, one could add a heteroatom source, e.g., phosphoric or sulfurous acid, to bring down the pH below 13, but above 6 to 8. The advantage of this use of the invention is that the pH may be adjusted without adverse effects since the phosphate or sulfite does not interfere with the etching process while forming the heteropoly compound.

It will be apparent to those skilled in the art having regard to this disclosure that other modifications of this invention beyond those embodiments specifically described here may be made without departing from the spirit of the invention. Accordingly, such modifications are considered within the scope of the invention as limited solely by the appended claims.

What is claimed is:

1. A neutral or near neutral pH etching solution for effectively etching molybdenum and tungsten comprising:
  - an aqueous ferricyanide ion solution, a soluble molybdate or tungstate, and an essential compound such that upon combination of said soluble molybdate or tungstate and said essential compound, a heteropoly compound is formed in which said essential compound contributes at least one heteroatom to said heteropoly compound.
2. The etching solution of claim 1 wherein said essential compound is phosphoric acid and said heteroatom is phosphorus.
3. The etching solution of claim 1 wherein said essential compound is sulfurous acid and said heteroatom is sulfur.
4. The etching solution of claim 1 wherein said soluble molybdate is sodium molybdate.
5. The etching solution of claim 4 wherein the pH of said solution is in the range of about 7 to 8.
6. The etching solution of claim 1 wherein said soluble tungstate is sodium tungstate.
7. The etching solution of claim 6 wherein the pH of said solution is in the range of about 6 to 8.
8. The etching solution of claim 1 further comprising a charge balancing species.
9. The etching solution of claim 8 wherein said charge balancing species is selected from the group consisting of sodium, potassium, and ammonium ions.
10. The etching solution of claim 1 wherein said etching solution is at room temperature.
11. A method of effectively etching molybdenum or tungsten from a composite material comprising molyde-

num or tungsten adhered to a base-sensitive material without damaging the material comprising the steps of: contacting the composite with a neutral or near neutral pH etching solution comprising:

an aqueous ferricyanide ion solution, a soluble molybdate or tungstate, and an essential compound such that upon combination of said soluble molybdate or tungstate and said essential compound, a heteropoly compound is formed in which said compound ingredient contributes at least one heteroatom to said heteropolycompound.

12. The method of claim 11 wherein said essential compound is phosphoric acid and said heteroatom is phosphorus.

13. The method of claim 11 wherein said essential compound is sulfurous acid and said heteroatom is sulfur.

14. The method of claim 11 wherein said soluble molybdate is sodium molybdate.

15. The method of claim 14 wherein the pH of said solution is in the range of about 7 to 8.

16. The method of claim 11 wherein said soluble tungstate is sodium tungstate.

17. The method of claim 16 wherein the pH of said solution is in the range of about 6 to 8.

18. The method of claim 11 further comprising a charge balancing species.

19. The method of claim 18 wherein said charge balancing species is selected from the group consisting of sodium, potassium, and ammonium ions.

20. The method of claim 11 wherein said etching solution is at room temperature.

21. The method of claim 11 further comprising the step of introducing ozone into said etching solution to rejuvenate said solution.

\* \* \* \* \*

**United States Patent** [19]  
**Choi et al.**

[11] **Patent Number:** **4,663,191**  
 [45] **Date of Patent:** **May 5, 1987**

[54] **SALICIDE PROCESS FOR FORMING LOW SHEET RESISTANCE DOPED SILICON JUNCTIONS**

4,563,805 1/1986 Scovell ..... 29/590  
 4,567,058 1/1986 Koh ..... 427/93  
 4,609,568 9/1986 Koh ..... 427/93

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*Primary Examiner*—John D. Smith  
*Attorney, Agent, or Firm*—Sughrue, Mion, Zinn, Macpeak, and Seas

[73] **Assignee:** International Business Machines Corporation, Armonk, N.Y.

[57] **ABSTRACT**

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[51] **Int. Cl.:** H01L 21/24

[52] **U.S. Cl.:** 427/93; 156/628; 156/656; 156/657; 427/99

[58] **Field of Search:** 427/93, 99; 156/628, 156/656, 657

[56] **References Cited**

**U.S. PATENT DOCUMENTS**

4,180,596 12/1979 Crowder ..... 427/93  
 4,332,839 6/1982 Levinstein ..... 156/656  
 4,337,476 6/1982 Fraser ..... 427/93  
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A process of forming a patterned silicide layer overlying a processed semiconductor substrate, the substrate having insulator regions and insulator-free regions on an exposed surface thereof, comprising the steps of: co-depositing silicon and a refractory metal on the exposed surface of the substrate to form a metal rich silicide thereon; annealing the metal rich silicide such that it reacts with the underlying insulator-free regions to form a reacted silicide without reacting with the underlying insulator regions; and exposing the substrate to a wet etchant which removes the unreacted portions of the metal rich silicide without removing the reacted silicide.

**11 Claims, 4 Drawing Figures**

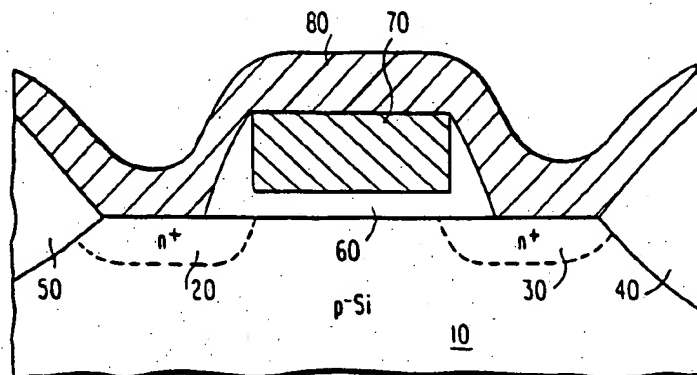


FIG. 1A

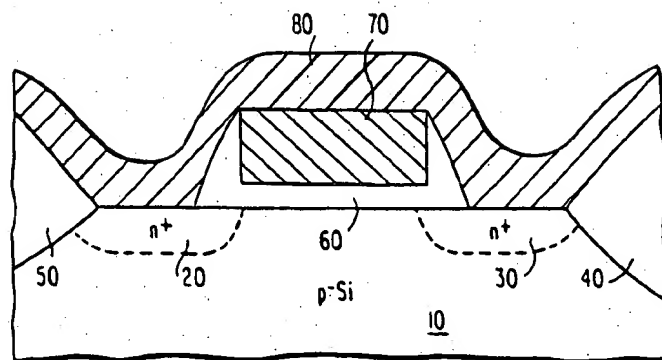


FIG. 1B

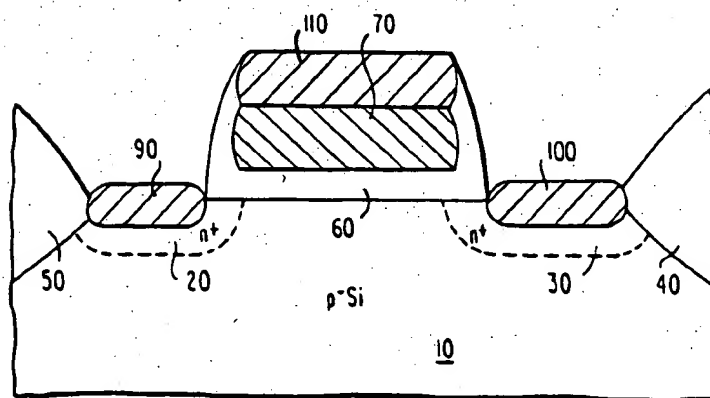


FIG. 2

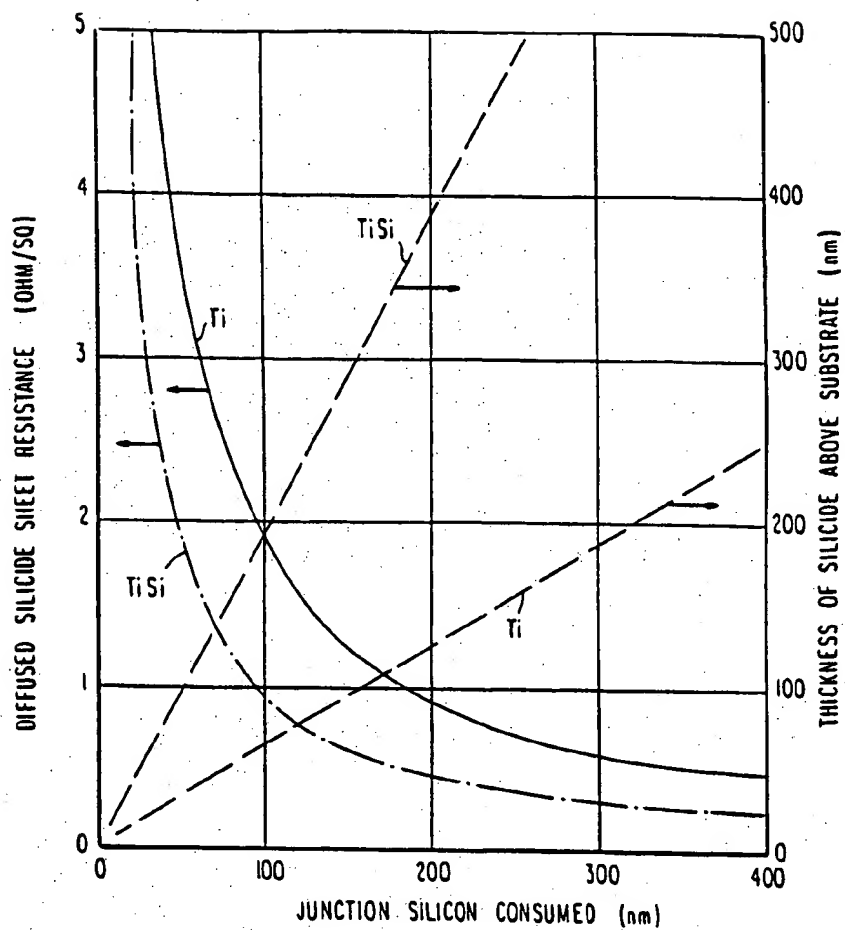
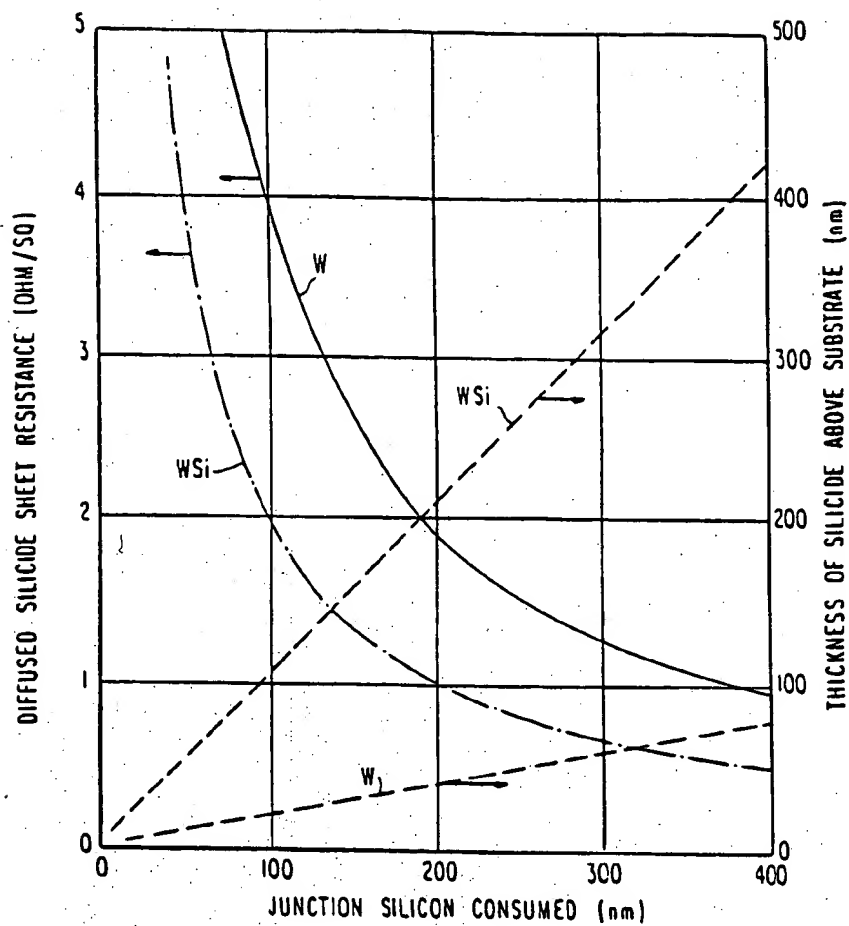


FIG 3



## SALICIDE PROCESS FOR FORMING LOW SHEET RESISTANCE DOPED SILICON JUNCTIONS

### BACKGROUND OF THE INVENTION

The present invention is concerned with providing a layer of certain metal silicides on a substrate; it is particularly advantageous for providing self-aligned metal silicide layers on semiconductor substrates such as doped silicon and doped polycrystalline silicon.

### FIELD OF THE INVENTION

The present invention is specifically contemplated as an improvement on the process of U.S. Pat. No. 4,180,596 Crowder et al, which patent is hereby completely incorporated by reference.

Polycrystalline silicon has in recent years been used to a great extent as the interconnection material in integrated circuits. It is stable at high temperatures and silicon dioxide can be chemically vapor deposited or thermally grown thereon.

An undesirable feature of polycrystalline silicon is its relatively high electrical resistance. For the reasons explained in Crowder et al, it would be desirable to decrease the sheet resistance of polycrystalline silicon interconnections in order to gain increased circuit speed.

It has been suggested that various refractory metals such as molybdenum and tungsten could be used in place of polycrystalline silicon. However, these metals oxidize during chemical vapor deposition of silicon dioxide and the resulting oxides are less stable than silicon dioxide, resulting in a reliability problem.

A number of attempts have been made to overcome the above problem including the process of Crowder et al. Crowder et al discusses a number of prior art references, for example, *IBM Technical Disclosure Bulletin*, Vol. 17, No. 6, Nov. 1974, pp. 1831-33; U.S. Pat. No. 3,381,182; French Pat. No. 2,250,198; and *Journal of the Electrochemical Society, Solid-State Science and Technology* "Fabrication and Thermal Stability of W-Si Ohmic Contacts", by V. Kumar, Feb. 1975, pp. 262-69.

Other references of interest include an article in *Proceedings of the 9th Conference on Solid-State Devices, Tokyo (1977)*, pp. 37-40 by Mochizuki et al; "Refractory Silicides for Low Resistivity Gates and Interconnects", 1979 *International Electron Devices Meeting*, pp. 454-57 by Murarka; "Properties of Sputtered Tungsten Silicide for MOS Integrated Circuit Applications", *Journal of the Electrochemical Society—Solid-State Science and Technology*, Feb. 1980, pp. 450-54; *IBM Technical Disclosure Bulletin*, Vol. 24, No. 12, May 1982, p. 6282 by Tu; U.S. Pat. No. 4,411,734; and U.S. Pat. No. 4,443,930.

As discussed in the above prior art, a silicide electrode is typically formed by depositing a layer of silicon, depositing a layer of a refractory metal (e.g., tungsten, molybdenum, etc.), and then annealing the two layers such that the silicide (e.g., tungsten silicide) is formed. Crowder improves on this basic process by co-depositing a refractory metal and silicon from separate evaporation sources to form the silicide. This enables a designer to precisely control the composition of the silicide.

In an article by S. Roberts entitled "Salicide Process for Silicide Wiring for CVD", *IBM Technical Disclosure Bulletin*, Vol. 26, No. 8, Jan. 1984, p. 4338, a layer of refractory metal is deposited on a substrate having isola-

tion regions such as semi-recessed silicon oxides. When the structure is annealed, the refractory metal interacts with the underlying silicon without reacting with the underlying oxide. Subsequently, the unreacted refractory metal on top of the oxide may be removed in a wet etch without removing the formed silicide. The process results in a self-aligned silicide (i.e., "salicide") because an electrode is formed between the recessed oxide areas without the use of a mask.

A problem with the above "salicide" process is that when the refractory metal reacts with the underlying silicon, an excessive amount of silicon is consumed. As device dimensions decrease, the ability to form so-called "shallow junctions", in which the thickness of the silicon beneath the gate electrode of an FET is minimized, becomes more important.

In a publication entitled "A New Device Interconnect Scheme For Sub-Micron VLSI" by Chen et al, 1984 *International Electron Devices Meeting*, pp. 118-119, it is suggested that a layer of metal can be deposited followed by a layer of silicon such that shallow junctions can be formed in a silicide process. However, this process is not self-aligned, i.e., a masking step is needed to photolithographically define the silicon layer prior to annealing to form the silicide.

### SUMMARY OF THE INVENTION

The present invention provides a process of forming a self-aligned silicide ("salicide") by a method which does not consume an excessive amount of the underlying silicon.

Specifically, a metal rich silicide is formed by co-deposition of a refractory metal and silicon on a substrate. As a consequence, upon annealing to form the desired silicide, only a small amount of silicon is consumed.

The major problem which the present invention solves is that using the etch compositions of the prior art, it has been extremely difficult to remove the unreacted metal rich silicide without simultaneously removing the reacted silicide.

In accordance with the present invention, it has been found that the unreacted metal rich silicide can be removed without removing the reacted silicide with certain combinations of metal-rich silicides and certain wet etchants.

One major object of the present invention is to provide a process of forming a patterned silicide layer overlying a processed semiconductor substrate where unreacted metal rich silicide can be removed without removing reacted silicide, which process is self-aligning, i.e., which does not require a photolithographic removal step.

A further major object of the present invention is to provide extremely shallow source/drain junction depths in semiconductor devices, for example, on the order of about 0.1 to about 0.3 microns or even as low as 0.05 to 0.15 microns.

Yet another object of the present invention is to provide electrical interconnections of low sheet resistance, for example, on the order of under about 5 ohms/sq. in combination with shallow source/drain junction depths as above exemplified.

These and other objects of the present invention will become clearer upon a reading of the following material.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A and 1B illustrates sequential cross-sectional views of one fabrication scheme for an integrated circuit employing the process of the present invention.

FIGS. 2 and 3 are plots of diffused silicide sheet resistance (ohms/sq.) versus junction silicon consumed (nm) versus thickness of the resulting silicide (nm), for deposited titanium versus deposited metal rich titanium silicide (FIG. 2), and for deposited tungsten versus deposited metal rich tungsten silicide (FIG. 3).

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The process of the present invention is applicable to forming films of the desired silicide on any substrate which is capable of withstanding the high temperatures employed in the co-evaporation process and which is adherent to the desired silicide.

The process is particularly advantageous in preparing integrated circuits and is of particular value when the substrate is silicon or polycrystalline silicon and is of most particular value in forming layers which are employed as an overlayer over doped polycrystalline silicon gate electrodes and as an overlayer directly over doped silicon diffused lines.

The general processing conditions of the present invention are firstly discussed and then a detailed discussion of the interrelationship between the metal rich silicides of the present invention and the etchants of the present invention which permit the metal rich silicide to be removed without the reacted silicide being removed will be presented.

It is to be noted that with respect to the general processing conditions of the present invention, i.e., other than the nature of the metal silicides and the etchants used, the conditions of Crowder et al are applied. They are briefly discussed below for purposes of self-containment.

The metal and silicon are typically vaporized under high vacuum and co-deposited on the substrate. The vacuum employed is typically on the order of about  $10^{-5}$  to  $10^{-6}$  Torr. A preferred method of heating is by electron beam evaporation preferably using separate electron beam guns for the silicon and the metal. The apparatus and conditions for the vacuum evaporation are known and will not be described.

It is preferred that the evaporation rate of the metal be on the order of 0.5 to 2 Angstroms per second, and that of silicon be on the order of 1 to 3 Angstroms per second, respectively, with specific rates being determined by the desired composition of the deposited metal-silicon mixture.

In addition to vacuum evaporation as above described, the metal and silicon can be deposited by a conventional sputtering operation or a conventional chemical vapor deposition operation, the conditions being well known in the art.

The substrate to be coated is usually maintained at a temperature between about room temperature and about 400° C., preferably between about 150° C. and 250° C. during coating.

Metals co-deposited with silicon in accordance with the present invention include titanium, cobalt, nickel, vanadium, tungsten, molybdenum, and we believe, zirconium will also be useful, and the like.

As deposited, the metal/silicon system can be represented by the formula  $MSi_x$ . With this representation, M

represents the metal and Si represents the silicon, "x" representing the atomic proportion of silicon.

Since the object of the present invention is to deposit an alloy, whether deposition is by vacuum evaporation, sputtering or chemical vapor deposition, x must be greater than 0. Normally, we have found that x should be a minimum of about 0.25; if x is less than about 0.25, one approaches the metal and the objects of the present invention are not met.

The maximum value for x will vary depending upon the metal involved.

For example, for titanium, zirconium, tungsten and molybdenum x would be a maximum of 1.0 whereas for cobalt, vanadium and nickel x would be a maximum of about 0.75.

The above values are as-deposited values; after annealing, all metal silicides will be in the reacted silicide form, which can be represented by the formula  $MeSi_2$ .

Typical as deposited alloys in accordance with the present invention include  $Ti_4Si_3$ ,  $TiSi_{1.0}$ ,  $Co_3Si_2$ ,  $V_3Si_2$ ,  $CoSi_{0.75}$  and  $WSi_{1.0}$ . At present,  $TiSi_{1.0}$  and  $CoSi_{0.75}$  appear most promising, and  $TiSi_{1.0}$  is most preferred.

After the desired amount of metal and silicon are deposited on the substrate, the substrate is removed and subjected to a high temperature heat treatment (annealing). Specifically, the coated substrate is heated in an inert atmosphere or vacuum. The only importance to the atmosphere is to exclude the presence of oxygen. Generally, for the metals titanium, zirconium, cobalt and nickel, a temperature of from about 550° C. to about 750° C. will be used, whereas for vanadium and tungsten a temperature of about 750° C. to about 900° C. will be used in a conventional furnace. If rapid thermal annealing is contemplated where a high intensity arc lamp is used, the upper limit can be lifted approximately 100° C. so that the upper limit of processing most preferably would be about 850° C. or 1,000° C., respectively, for these groups of metals. The maximum temperature generally is selected to avoid excessive grain growth in the silicide.

The time of annealing is not critical so long as the objective of annealing, i.e., complete reaction to the desired silicide, is achieved. Based on our experience to date, it appears that conventional furnace annealing for about one-half hour to about one hour will achieve this result and rapid thermal annealing for about 10 to about 200 seconds also provides the desired result. The time is inversely related to temperature.

The inert atmosphere can be freely selected; examples include argon, helium and hydrogen. The inert atmosphere should be free of substances which cause the formation of carbides, oxides or nitrides of the metal during heating.

If a vacuum is utilized, a pressure of at least  $10^{-5}$  Torr is usually sufficient.

If an inert atmosphere is utilized, the objective is to prevent backflow of oxygen into the system (typically from the ambient); as a consequence, if an inert gas is used, the pressure and/or rate of flow is merely sufficient to prevent the backflow. If a vacuum is used, the degree of vacuum is merely sufficient to prevent the presence of oxygen in the system. As a consequence, the pressure of operation is not overly important.

In the situation where an inert atmosphere is used in combination with titanium, normally nitrogen is added, typically in an amount on the order of from about 0.5 to about 5 volume %, to prevent the lateral spread of silicide onto oxide areas.



Following the above procedure, the etching of the present invention is conducted to remove the metal rich silicide without removing the reacted silicide.

After the above removal step, if desired, the coated substrate can be subjected to various conventional procedures as described in Crowder et al.

Following deposition and annealing, the major objective of the present invention is, of course, to remove the metal silicide from areas where the same is not desired but to permit substantially complete retention of the silicide over areas where the same is desired.

It has been discovered, in accordance with the present invention, that wet peroxide etching baths, of a basic or acidic nature, permit this to be achieved.

Wet basic peroxide etchant baths are effective with titanium, zirconium, tungsten and molybdenum silicides; acidic peroxide baths are effective with cobalt, vanadium and nickel silicides.

The wet etchants of the present invention will always comprise an aqueous system which will include water and a source of peroxide. The source of the base or acid can vary.

For basic wet etchants, the pH will normally be about 11 to about 12. At present, the preferred base is ammonium hydroxide; the reason for this is that sodium hydroxide or potassium hydroxide tend to attack oxide present.

For acidic wet etchants, the pH will normally be from about 1 to about 2, i.e., the systems are highly acidic. Both hydrochloric and sulfuric acids are useful, but care should be taken in utilizing nitric acid or hydrofluoric acid since the same will tend to attack oxide present.

The acidic or basic peroxide etchants of the present invention are, as indicated, highly concentrated. For example, excellent results are obtained with a 1:1:1 volume solution of hydrogen peroxide:acid/base:water whereas with a 1:1:2 volume solution of the same components, only a partial etch is obtained.

Thus, it is most preferred that the hydrogen peroxide and acid/base each be used in at least an equal volume amount with respect to added water, preferably greater.

The acids or bases used in the present invention are normally used as saturated solutions in water. The hydrogen peroxide is generally used as available, i.e., a 30% aqueous solution (volume).

The maximum amounts of acid/base or hydrogen peroxide do not appear overly important, but as the amount of water added is increased to dilute the system to an amount much greater than about 1 part by volume added water with 1 part by volume acid/base and 1 part by volume hydrogen peroxide, etching results decrease in acceptability.

Both the basic wet etchants and acidic wet etchants in accordance with the present invention provide a high etch ratio between metal silicide reacted with underlying monocrystalline or polycrystalline silicon and unreacted metal silicide overlying silicon dioxide areas.

The pressure of etching is not overly important; normally we just use ambient pressure, but if one were willing to go to superatmospheric conditions or subatmospheric conditions, we at present see no basic change in processing conditions. Ambient conditions are most convenient.

The temperature of etching should be maintained from about 55° to about 85° C.

The time of etching is not critical since the etching process is autocatalytic, i.e., the rate of etching in-

creases as process time increases. As a general rule, from about 5 to about 10 minutes is sufficient for etching in accordance with the present invention. The time of etching is not meant to be critical nor is it considered limitative on the present invention.

The time of etching will obviously have to be correlated with the thickness of the silicide film involved, with thicker films requiring longer times.

The thickness of the silicide film is set by design requirements. For example, the thickness of the silicide will be determined by the resistivity of the remaining silicide and the amount of silicon which is to be consumed, i.e., the depth of the ultimate junction which is to be obtained.

A typical basic etching solution would comprise equal volume parts of  $\text{NH}_4\text{OH}-\text{H}_2\text{O}_2$  (30 vol %)- $\text{H}_2\text{O}$ , and a typical acidic etching solution would comprise equal volume parts of  $\text{HCl}-\text{H}_2\text{O}_2$  (30 vol %)- $\text{H}_2\text{O}$ . Both of these solutions are much more concentrated than the 1:1:5 solutions typically used in conventional silicide processes. We have found that these conventional wet etch solutions do not provide favorable results.

In FIG. 1A, a typical p-type silicon substrate is represented by the numeral 10. Implanted therein by any conventional means are  $n^+$  source and drain regions 20 and 30, respectively.

$\text{SiO}_2$  isolation regions 40 and 50 are shown, the same being formed in a conventional manner.  $\text{SiO}_2$  region 60 is shown grown on the silicon substrate, again growth being in a conventional manner by chemical vapor deposition or thermal growth with etching of the  $\text{SiO}_2$  area being performed photolithographically in a conventional manner. Polysilicon gate 70 is also shown in FIG. 1. To this stage, processing is conventional.

After the above conventional procedures, the metal silicide of the present invention is deposited, as illustrated by layer 80. It is to be noted that the metal silicide completely covers  $\text{SiO}_2$  areas 40 and 50 and polysilicon gate 70 as shown in FIG. 1A.

Following deposition of the metal silicide, annealing in accordance with the present invention is conducted and, following annealing in accordance with the present invention, wet etching is conducted using a basic or acidic aqueous peroxide solution.

Following annealing and etching, the structure of FIG. 1B results. As can be seen from FIG. 1B, deposited metal silicide over the  $\text{SiO}_2$  areas 40 and 50 has been removed (since there is no reaction with the silicon oxide thereunder), but metal silicide remains in areas where (in this instance) silicon was available for reaction, specifically, at areas 90 and 100 (overlying the source and drain areas 20 and 30) and over polysilicon gate 70 as shown by remaining metal silicide 110.

In accordance with the present invention, in areas where metal silicide does not react with the underlying silicon oxide, the same is substantially completely removed.

With reference to FIGS. 2 and 3, it is easily seen that for the same amount of junction silicon consumed a significantly lower sheet resistance is obtained with deposited alloys in accordance with the present invention as compared to that obtained with pure metal deposition. FIG. 2 compares pure titanium deposition with  $\text{TiSi}_2$  deposition and FIG. 3 compares pure tungsten deposition with  $\text{WSi}_2$  deposition.

In accordance with the present invention, a 100% decrease in achievable sheet resistance for the silicide

junctions can be obtained as compared to the pure metal, for example, with  $\text{TiSi}_{1.0}$  as compared to pure Ti.

Conversely, for comparable sheet resistances, only half of the required junction silicon consumed is observed with, e.g.,  $\text{TiSi}_{1.0}$  alloy films in accordance with the present invention as compared to that observed with pure Ti deposition, thereby providing a significantly higher margin of safety with respect to junction shorting. This permits shallower doped silicon junctions, an important factor with emerging VLSI technology.

A consequence of the fact that less junction silicon is consumed is that devices formed in accordance with the present invention do not illustrate non-ohmic behavior.

The following specific embodiments illustrate the benefits obtained per the present invention in more detail.

#### Case I—Titanium Metal Deposition—Conventional Salicide Process

50 nm of titanium (Ti) metal will react with 113.5 nm of junction silicon (Si) to form 118.5 nm of titanium silicide ( $\text{TiSi}_2$ ). This should yield a sheet resistance, for the  $\text{TiSi}_2$ , of 1.26 ohms/square (based upon a specific

that obtained with Ti metal deposition. This is an example of a most important benefit of the present invention, i.e., the ability, by use of the deposited alloy, to obtain more shallow junctions for a specified salicided junction resistance.

#### Case III— $\text{TiSi}_x$ Alloy Deposited For Fixed Junction Depth and Reduced Junction Resistance

By doubling the amount of deposited titanium and silicon the same net junction depth will be produced as in Case I (i.e., 113.5 nm). However since the final silicide thickness is twice that obtained in Case I, the sheet resistance will be reduced by one-half (i.e., 0.63 ohms/sq.). Thus, the present invention also gives a designer the flexibility of selectively decreasing the sheet resistance without compromising shallow junctions. To achieve a 0.63 ohms/sq. sheet resistance in Case I, the final silicon junction would have to be 227 nm, i.e., double that achieved by utilizing the present invention.

The above examples are summarized in the following Table, along with similar cases for saliciding with cobalt (for Case II,  $x \approx 0.75$ ).

TABLE

Case	Metal	Si/Me Ratio (1)	MeSi <sub>2</sub> Ratio (2)	Deposited Film Si/Me Ratio (3)	Deposited metal	Deposited silicon	Thickness (nm)		Remaining junction silicon (4)	Salicided Junction Resistance ohms/sq (5)
							Original junction thickness	Junction silicon consumed		
I	Ti	2.27	2.37	0	50	0	227	113.5	113.5	1.26
II	Ti	2.27	2.37	1.0	50	56.75	113.5	56.75	56.75	1.26
III	Ti	2.27	2.37	1.0	100	113.5	227	113.5	113.50	0.63
I	Co	3.66	3.56	0	31	0	227	113.5	113.5	1.54
II	Co	3.66	3.56	0.75	31	42.5	142	71	71	1.54
III	Co	3.66	3.56	0.75	50	68	230	115	115	0.96

(1) Volume (film thickness) ratio of metal to silicon needed to form the final  $\text{MeSi}_2$  silicide

(2) Final  $\text{MeSi}_2$  silicide volume (film thickness) ratio to deposited metal volume (thickness)

(3)  $\text{MeSi}_2$  ratio for maximum silicon that will yield a silicide reaction as per the invention

(4) Based upon experimentally determined rule that no more than one-half of the original junction is consumed for silicide formation

(5) Resistivity of  $\text{TiSi}_2 = 15$  micro-ohm-cm;  $\text{CoSi}_2 = 17$  micro-ohm-cm.

resistivity for the  $\text{TiSi}_2$  of 15 micro-ohm-cm). Under these conditions, the remaining silicon junction will be 113.5 nm. This would be the optimum result achievable using a conventional self-aligned silicide processes.

This amount of Ti can be used with pre-salicided doped Si junctions ranging down to 0.25 microns deep, based upon the following characteristics of optimized salicided junctions:

(1) the junction should provide ohmic contact between the salicided layer and remaining junction Si that is not consumed by the Ti;

(2) the junction should not exhibit excessive reverse bias diode leakage, normally exhibited by good non-salicided diodes of the same thickness as the salicided diodes and an equivalent dopant profile provide; and

(3) the junction should exhibit normal forward bias characteristics.

It has been determined experimentally that up to one-half of the original junction Si can be consumed, during saliciding, and still yield the above junction diode properties.

#### Case II— $\text{TiSi}_x$ ( $x \approx 1$ ) Alloy Deposit

The deposition of the above alloy (i.e., 50 nm of titanium, 56.75 nm of silicon) will result in the consumption of only one-half as much (i.e., 56.75 nm) junction Si as compared with Case I, yielding a junction only one-half as deep (i.e., 56.75 nm). The same silicide resistivity will be observed since the final  $\text{TiSi}_2$  thickness is similar to

Having thus described general aspects of the invention, the following currently preferred best modes of practicing the invention are offered.

#### EXAMPLE 1

Silicon dioxide was grown in a conventional manner on a conventional p-type silicon substrate, and then polysilicon was deposited thereon using conventional techniques. Following polysilicon deposition, photolithographic etching was conducted in a conventional manner to define the polysilicon gate electrode. This in turn defines the source and drain regions. The source and drain regions were then doped with arsenic to a doping profile level of  $10^{20}/\text{cm}^2$  at the silicon surface with a junction depth of 300 nm, and the remaining silicon dioxide was then removed.

Processing as above is conventional in the art.

After the above procedure, the intermediate device was introduced into a vacuum evaporation furnace which was maintained at a pressure of  $10^{-6}$  Torr. Using electron beam evaporation, a source of pure titanium and a source of pure silicon were evaporated to form a titanium-silicon alloy over the complete surface of the intermediate device using the following conditions: Ti evaporation rate = 2 Angstroms/sec., Si evaporation rate = 2.27 Angstroms/sec.

The alloy had the composition  $\text{TiSi}_{1.0}$ ; the thickness of the  $\text{TiSi}_{1.0}$  was 106.75 nm (50 nm Ti plus 56.75 nm Si).

Following deposition of the  $\text{TiSi}_{1.0}$ , the intermediate device was introduced into a furnace, whereafter the inert gas forming gas containing 10 vol %  $\text{H}_2$  plus 90 vol %  $\text{N}_2$  was flowed through the furnace; the furnace temperature was raised to  $650^\circ\text{C}$ . and annealing was conducted at that temperature for 30 minutes.

The intermediate device was removed from the furnace and then etched in an etchant comprising (all parts are by volume) 1 part  $\text{NH}_4\text{OH}$ , 1 part  $\text{H}_2\text{O}_2$  (30 vol %) and 1 part  $\text{H}_2\text{O}$ , heated to  $75^\circ\text{C}$ . Etching was conducted for 5 minutes at the above conditions. Etching was otherwise at ambient conditions.

The intermediate device was then removed from the etch bath.

The unreacted  $\text{TiSi}_{1.0}$  had been completely removed over the silicon dioxide areas, and yet the reacted  $\text{TiSi}_2$  remained over the source and drain regions and over the polysilicon gate electrode.

The resulting junction depth was 56.75 nm.

#### EXAMPLE 2

The procedure of Example 1 was followed except for evaporating cobalt and silicon to yield as deposited  $\text{CoSi}_{0.75}$  and annealing was at  $650^\circ\text{C}$ . The etch bath used was 1 part  $\text{HCl}$ , 1 part  $\text{H}_2\text{O}_2$ , and 1 part  $\text{H}_2\text{O}$  heated to  $75^\circ\text{C}$ .

Similar results were obtained.

While there have been described what are at present considered to be the preferred embodiments of this invention, it will be obvious to those skilled in the art that various changes and modifications can be made therein without departing from the invention, and it is, therefore, intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. A process of forming a patterned silicide layer overlying a processed semiconductor substrate, the substrate having insulator regions and insulator-free regions on an exposed surface thereof, comprising the steps of:
  - co-depositing silicon and a refractory metal on the exposed surface of the substrate to form a metal rich silicide of the formula  $\text{MSi}_x$  thereon, wherein  $0.25 \leq x \leq 1.0$ ;
  - annealing the metal rich silicide such that it reacts with the underlying insulator-free regions to form a reacted silicide without reacting with the underlying insulator regions; and

exposing the substrate to a concentrated basic peroxide etchant which removes the unreacted portions of said metal rich silicide without removing said reacted silicide.

2. The process of claim 1, wherein said refractory metal is selected from the group consisting of titanium, zirconium, tungsten and molybdenum.

3. The process of claim 1, wherein said refractory metal is titanium.

4. The process of claim 1, wherein said insulator-free regions comprise monocrystalline or polycrystalline silicon, and wherein said insulator regions comprise silicon dioxide.

5. The process of claim 1, wherein said etchant has a pH of about 11 to about 12.

6. The process of claim 1, wherein said etchant consists essentially of a 1:1:1 volume solution of ammonium hydroxide, hydrogen peroxide and water.

7. A process of forming a patterned silicide layer overlying a processed semiconductor substrate, the substrate having insulator regions and insulator-free regions on an exposed surface thereof, comprising the steps of:

co-depositing silicon and a refractory metal on the exposed surface of the substrate to form a metal rich silicide of the formula  $\text{MSi}_x$  thereon,  $0.25 \leq x \leq 0.75$ ;

annealing the metal rich silicide such that it reacts with the underlying insulator-free regions to form a reacted silicide without reacting with the underlying insulator regions; and

exposing the substrate to a concentrated acidic peroxide etchant which removes the unreacted portions of said metal rich silicide without removing said reacted silicide.

8. The process of claim 7, wherein said refractory metal is selected from the group consisting of cobalt, vanadium and nickel.

9. The process of claim 7, wherein said insulator-free regions comprise monocrystalline or polycrystalline silicon, and wherein said insulator regions comprise silicon dioxide.

10. The process of claim 7, wherein said etchant has a pH of about 1 to about 2.

11. The process of claim 2, wherein said etchant consists essentially of a 1:1:1 volume solution of a member selected from the group consisting of hydrochloric acid and sulfuric acid, in combination with hydrogen peroxide and water.

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WITH QUATERNARY AMMONIUM  
HYDROXIDE-BASED AQUEOUS CLEANING  
COMPOSITIONS**(21) **Appl. No.: 09/096,840**(22) **Filed: Jun. 12, 1998****Publication Classification**(76) **Inventors: KRISHNA G. SACHDEV,  
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(US)**(51) **Int. Cl.<sup>7</sup> ..... C11D 17/08**(52) **U.S. Cl. .... 510/177; 510/415**(57) **ABSTRACT**

This invention relates to cleaning organic polymer-metal composite material from screening masks and associated accessories used for printing a conductive paste pattern on microelectronic components, such as, for example, ceramic green sheets in the production of semiconductor packaging substrates. More particularly, this invention is concerned with the aqueous cleaning of screening paste residue from masks and other paste screening and processing equipment using water-based alkaline cleaning compositions comprising an organic quaternary ammonium hydroxide as the primary basic active ingredient to provide a more environmentally friendly alternative to non-aqueous organic solvents-based cleaning.

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# REMOVAL OF SCREENING PASTE RESIDUE WITH QUATERNARY AMMONIUM HYDROXIDE-BASED AQUEOUS CLEANING COMPOSITIONS

## FIELD OF THE INVENTION

[0001] This invention relates to cleaning organic polymer-metal composite materials from screening masks and associated accessories used in printing conductive paste patterns on ceramic green sheets in the production of substrates for semiconductor packaging. More particularly, this invention is concerned with the aqueous cleaning of screening paste residue from masks and other screening equipment using water-based alkaline cleaning compositions comprising an organic quaternary ammonium hydroxide as the primary basic active ingredient to provide a more environmentally friendly alternative to non-aqueous organic solvents based cleaning.

## BACKGROUND OF THE INVENTION

[0002] In the fabrication of multilayer ceramic (MLC) substrates for packaging semiconductor devices, conductive metal patterns are screened onto individual ceramic green sheets through a mask, such as, a metal mask. This screening can be done, such as, by extrusion printing using at least one nozzle, or by screen printing through an emulsion mask employing a non-pressurized paste squeegee method, etc. After screening, the green sheets are assembled and aligned, laminated and then sintered.

[0003] The fabrication processes and equipment used to produce multilayer ceramic packages with paste-screened internal metallization are well known in the art.

[0004] However, the fabrication of advanced ground rule electronic packaging structures requires the printing of closely spaced conductive metal patterns utilizing metal masks that have a high density of fine pitch etched features. It has been observed that in the case of the masks having closely spaced features, there is a problem with paste residue build-up in and around the mask features in addition to the residue on the top and bottom surface of mask. This requires that the masks, especially the metal masks be cleaned after one or more screening passes to remove such residue to eliminate/minimize the possibility of defects in subsequently screened patterns, thereby preventing product yield loss. Furthermore, removing paste residue on masks is more critical in the case of finer pitch etched features.

[0005] Conductive pastes used in screening processes for the delineation of wiring and via metallurgy pattern or for use in the application of solder-based paste patterns onto electronic components, basically comprise metal particles dispersed in an organic binder and solvent vehicle along with wetting agents, dispersants/surfactants, plasticizers, and other additives as rheology modifiers, thickening agents, antioxidants, and coloring agents which are all well known ingredients in paste compositions for the fabrication of electronic components.

[0006] Additionally, selection of conductive screening pastes which are based on a variety of metal/polymer binder/solvent vehicle systems is dictated by several considerations, viz, the requirement for a particular circuit pattern, the drying characteristics of the paste, the match of

paste shrinkage with that of the ceramic, and the overall compatibility of the paste with the green sheet materials, to name a few.

[0007] The most commonly used conductive pastes in multilayer ceramic fabrication are based on molybdenum or tungsten metal powder dispersed in an organic binder, such as, for example, ethyl cellulose, polymethylmethacrylate and the like, or polyhydrocarbon based thermoplastic resins in a high boiling organic solvent vehicle. Other conductive paste types employed in multilayer ceramics can be based on copper, gold or nickel as the metal constituent. Because of the variety and complex chemical make-up of polymer/metal dispersions, it is required that the mask cleaning medium and process selected be such that it provides complete and efficient cleaning of paste residue on masks and associated equipment regardless of the paste characteristics in terms of wettability, solubility, polarity, etc.

[0008] Recently, several water-based cleaners have become commercially available and many aqueous detergent compositions have been described in the patent literature, for example, for cleaning laboratory glassware, and printed circuit board assemblies to remove soldering flux, oil/grease, and other organic residues invariably formed during bonding and assembly processes. These are generally based on a combination of surfactants in water and/or alkaline detergent compositions comprising alkali metal salts as sodium metasilicate, sodium carbonate, tribasic sodium phosphate, sodium tripolyphosphate, and combinations thereof, and highly alkaline solutions based on alkali metal salts, alkali metal hydroxides, and mixtures thereof with alkanolamines; and microemulsion cleaners comprising an aqueous solution of surface active agents with detergent compositions and a water-insoluble organic solvent.

[0009] U.S. patent application Ser. No. \_\_\_\_\_, filed on May \_\_\_\_\_, 1998, Attorney Docket No. FI9-97-244, entitled "AQUEOUS QUATERNARY AMMONIUM HYDROXIDE AS A SCREENING MASK CLEANER", assigned to the assignee of the instant Patent Application, and the disclosure of which is incorporated herein by reference, discloses one such solution by using an aqueous quaternary ammonium hydroxide as a more environmentally friendly alternative to non-aqueous solvents for cleaning of masks, such as, a screening mask.

## PURPOSES AND SUMMARY OF THE INVENTION

[0010] The invention is a novel process for removing screening paste residue with aqueous, alkaline cleaning compositions based on quaternary ammonium hydroxide as the common active ingredient of these compositions.

[0011] Therefore, one purpose of this invention is to provide a method of cleaning paste screening masks and associated screening equipment using aqueous-based alkaline cleaning compositions.

[0012] Another purpose of this invention is to provide aqueous alkaline compositions based on organic quaternary ammonium hydroxide and a method of cleaning masks and other screening accessories with these compositions.

[0013] Yet another purpose of this invention is to provide an aqueous cleaning method using quaternary ammonium hydroxide based alkaline solution for removing paste resi-

due from masks and other screening accessories which utilizes a minimum volume of cleaning solution, conserves water, and reduces waste.

[0014] Yet another purpose of this invention is to provide an aqueous cleaning method for paste screening masks where it is practical to recover metals from the solid waste.

[0015] Still yet another purpose of this invention is to provide an aqueous cleaning method using quaternary ammonium hydroxide-based compositions which have no detrimental effect on screening equipment including metal masks, emulsion masks, screening nozzles, squeegee blades, polymer adhesives used in mask assembly, cleaning tool contacting surfaces, etc.

[0016] Therefore, in one aspect this invention comprises a composition for removing at least a portion of a screening paste residue from at least one paste screening object with at least one aqueous alkaline composition comprising at least one quaternary ammonium hydroxide as at least one component of said composition.

[0017] In another aspect this invention comprises a cleaning apparatus comprising:

[0018] (a) at least one means for immersing at least one screening object having screening paste residue on said screening object in at least one container;

[0019] (b) wherein said container comprises at least one aqueous alkaline composition having at least one quaternary ammonium hydroxide as at least one component of said composition;

[0020] (c) wherein said aqueous alkaline composition is subjected to at least one means of mechanical agitation;

[0021] (d) said at least one means of mechanical agitation also causes separation of at least a portion of said paste residue from said screening object; and

[0022] (e) at least one means of rinsing said screening object with water after cleaning with said aqueous alkaline solution, followed by at least one means of drying said screening object after said cleaning and rinsing operation.

[0023] In yet another aspect this invention comprises a cleaning apparatus comprising:

[0024] (a) at least one means for pressure spraying at least one solution onto at least one screening object having screening paste residue on said screening object; and

[0025] (b) wherein said at least one solution comprises at least one aqueous alkaline composition having at least one quaternary ammonium hydroxide as at least one component of said composition.

[0026] The features of the invention believed to be novel and the elements characteristic of the invention are set forth with particularity in the appended claims. The invention itself, however, both as to organization and method of operation, may best be understood by reference to the detailed description which follows:

#### DETAILED DESCRIPTION OF THE INVENTION

[0027] This invention is concerned with a method of removing paste residue from screening masks and ancillary

equipment used in screening conductive paste patterns on ceramic green sheets in the manufacture of multilayer ceramic substrates. This invention is particularly concerned with removing polymer-metal/inorganic paste residue from screening masks using aqueous cleaner compositions containing tetramethyl ammonium hydroxide and related organic quaternary ammonium hydroxides as such or in combination with additives for modifying wettability, specifically, surfactants and/or water soluble organic solvents, to provide a more environmentally friendly alternative to organic solvents.

[0028] The manufacture of semiconductor packaging products, such as multilayer ceramic substrates, typically employs the technique of conductive pattern screening onto ceramic green sheets through a mask, such as, a metal mask, using a variety of polymer/metal composite pastes to delineate conductive patterns for the desired circuitry. In this process, some paste residue accumulates in and around the fine pitch etched features of the mask, particularly on the underside, in addition to that on the surface of the mask. The entrapped residue must be removed if the mask is to be reused which involves cleaning after one or more screening passes depending on whether the paste is fast drying or slow drying as otherwise the residue can cause defects in subsequently screened conductive patterns. The particular combination of a polar and/or non-polar polymer binder and solvent vehicle system selected for dispersing the metal powder determines the solubility and wettability characteristics of the resulting paste which may range from hydrophilic to lipophilic and which may be fast drying or slow drying.

[0029] Selection of conductive screening pastes that are based on a variety of metal/polymer binder/solvent vehicle system is dictated by several considerations, viz., the requirement for a particular circuit pattern, drying characteristics, the match of paste shrinkage with that of the ceramic, and the overall compatibility of the paste with the green sheet materials for the necessary wettability and adhesion.

[0030] Screening masks are typically made of metal, such as, etched Mo masks, electroform masks, and emulsion masks for silk screening, such as, for example, stainless steel mesh with at least one photoresist coating of a suitable emulsion such as those based on polyvinyl alcohol-polyvinylacetate/polyacrylic-polyester type emulsion coatings.

[0031] The present invention provides a method for cleaning masks and other screening accessories using aqueous tetramethyl ammonium hydroxide-based alkaline cleaning compositions as a more environmentally friendly alternative to organic solvents for the effective cleaning of screening paste residue from masks and associated screening equipment regardless of the paste type.

[0032] Aqueous tetramethyl ammonium hydroxide (TMAH) is widely used in the semiconductor industry as a metal-ion-free resist developer in lithographic processes for integrated circuit device fabrication. Semi-aqueous cleaning compositions containing TMAH for removal of baked photoresist residues, and for cleaning semiconductor wafers and wafer carriers have been known. For example, U.S. Pat. No. 5,407,788 (Fang) describes the use of tetramethyl ammonium hydroxide (TMAH) in a non-aqueous solvent for stripping cured patterns of negative resist; U.S. Pat. No.

5,350,489 (Muraoka) is concerned with the use of quaternary ammonium hydroxide solutions for cleaning plastic molded items used in chemical analysis and wafer carriers to remove impurities of fine particles and fats and oils; and U.S. Pat. No. 5,466,389 (Iardi) is concerned with cleaning silicon wafers using aqueous cleaning compositions having 8-10 pH comprising TMAH and related organic bases or alkali metal hydroxides in combination with surfactants, buffering agents for adjusting pH to less than 10; U.S. Pat. No. 4,592,856 (Kobayashi) is concerned with removing oil/grease and resinous contaminants from the surface of plastic articles and molding equipment for eye glass lenses and optical instruments using detergent compositions comprising TMAH or 2-hydroxyethyl trimethyl ammonium hydroxide (Choline) in chlorinated solvents as perchloroethylene, 1,1,1-trichloroethane, methylene chloride, an ionic/non-ionic surfactant and methyl alcohol.

[0033] As stated earlier, the polymer/metal pastes that are used for defining via and wiring metallurgy patterns on ceramic green sheets are comprised of metal constituents, such as, molybdenum, copper, tungsten, some may contain nickel, gold, palladium, platinum and silver, which may include inorganic fillers such as glass, ceramic powder, or glass frit, all dispersed in an organic polymer binder and a high boiling solvent vehicle along with additives including dispersants, rheological control agents as thickening agents suitable for a particular screening application, antioxidants, coloring agents, etc.

[0034] The invention may also be used to clean masks and screens which are used in the application of solder pastes for various microelectronic components.

[0035] Representative polymer binder systems for molybdenum paste include: cellulosic polymers, for example, ethylcellulose, acrylate polymers such as polymethylmethacrylate, and polyhydrocarbon resins which are all hydrophobic, or the binder can be water soluble, for example, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, carboxymethyl cellulose, and the like.

[0036] The preferred high boiling solvent vehicle having a low evaporation rate in paste dispersions are ester-alcohol and glycol-ether type solvents such as 2,2,4-trimethylpentane diol, 1,3, monoisobutylate (Texanol), diethylene glycol monomethylether acetate, diethylene glycol monobutylether acetate or butyl carbitol acetate (BCA), and the like.

[0037] Depending on the solvent vehicle system used, the paste can be polar or non-polar, hydrophilic or lipophilic, and have differences in affinity and adhesive characteristics for a metal mask surface in addition to having differences in drying rate, which all affect the removal of paste residue by a particular cleaning medium.

[0038] According to this invention, it has been found that paste build-up in and around the mask features in the screening process can be readily removed by ultrasonic agitation in a heated aqueous alkaline solution comprising quaternary ammonium hydroxide, specifically, tetramethyl ammonium hydroxide (TMAH) as one of the active ingredients which may contain surface tension lowering additives, for example, surfactants and/or water soluble organic solvents, alkali metal hydroxide and alkali metal salts, and optionally one or more corrosion inhibitor. Minimum effec-

tive pH for the quaternary ammonium hydroxide-based aqueous cleaning solutions described here is greater than 11.5, preferably between about 11.9 and about 12.9.

[0039] The exact paste composition is not critical, any residue from screening pastes comprising electrically and/or thermally conductive ingredients in an organic polymeric binder and an organic solvent vehicle along with dispersing agent can be cleaned according to the method described here.

[0040] Ultrasonic cleaning is preferred over a spray wash as a multiple number of masks can be cleaned simultaneously in the same solution providing waste minimization, cost benefit, and reduction in water consumption. Although other means of mechanical agitation and pressurized spray also provide effective cleaning, these are not found suitable with surfactant carrying compositions even when the surfactant added is a low-foam type because of foam formation, which dampens the mechanical impact of pressurized spray.

[0041] In another embodiment of this invention, TMAH-based aqueous alkaline cleaning solutions may include alkali metal hydroxide such as sodium hydroxide, potassium hydroxide and/or alkali metal salts, such as, sodium carbonate, sodium sesquicarbonate, and/or potassium carbonate. These solutions may also include alkali metal silicates, for example, sodium silicate, potassium silicate, and/or sodium phosphate, sodium tripolyphosphate as detergency enhancing additives, and optionally one or more corrosion inhibitors.

[0042] Aqueous cleaning compositions comprising TMAH in conjunction with a non-ionic surfactant and/or a water soluble environmentally suitable organic solvent are especially effective with the ultrasonic cleaning of heavy paste residue from extrusion heads, paste nozzles, paste applicators, and other screening accessories.

[0043] Various quaternary ammonium hydroxides preferred for aqueous alkaline cleaning solutions according to this invention include: tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, tetrabutyl ammonium hydroxide, trimethyl-2-hydroxyethyl ammonium hydroxide (Choline), triethyl-2-hydroxy ethyl ammonium hydroxide, ethyltrimethyl ammonium hydroxide, methyl tri-(2-hydroxyethyl) hydroxide and the like. These solutions may also include organic amine bases such as those selected from the group alkanolamines, for example, 2-ethanolamine, diethanolamine, 1-amino-2-propanolamine, and the like.

[0044] Water soluble organic solvents selected for blending with TMAH-based aqueous solutions for paste residue removal are presently exempt from environmental regulations, particularly these solvents are not in the category of Hazardous Air Pollutants nor are these among the SARA Title-III reportable compounds or suspected carcinogens.

[0045] Representative solvent candidates suitable for the purpose of this invention include: dipropylene glycol alkyl ethers, for example, dipropylene glycol monomethyl ether, dipropylene glycol monobutyl ether, tripropylene glycol monomethyl ether, 3-methoxy-1-butanol, benzyl alcohol, and the like.

[0046] Surfactants which may optionally be added to aqueous alkaline solutions for example are non-ionic surfactants selected from the group, comprising low foam

linear long chain alcohol ethoxylates, typically, dodecyl alkyl ethoxylates, nonylphenoxy poly(ethyleneoxy) ethanol, octyl phenoxy-polyoxy ethanol; EO/PO polymers, such as, polyoxyethylene-polyoxypropylene block co-polymers at varying composition of EO/PO blocks; fluorinated polyoxyethylene alkanols, such as, Fluorad 171; and alkyl polyglycosides surfactants, for example, D-glucose-decyloctyl polyether ether oligomers. These surfactants are well known in the art and are commercially available as concentrates in a polypropylene glycol or polyethylene glycol-water mixture. In addition to these, ionic and amphoteric surfactants, defoamers and corrosion inhibitors may also be added if needed.

[0047] Unless specified otherwise, the percentages given in this patent application are in vol % (volume percent) and in wt % (weight percent).

[0048] According to one preferred embodiment of this invention, quaternary ammonium hydroxide-containing aqueous solutions that are effective in cleaning paste residue from screening masks and associated equipment comprise the following:

[0049] (a) An aqueous solution of tetramethyl ammonium hydroxide (TMAH) having between about 0.5 to about 5 wt % TMAH based on  $(\text{CH}_3)_4\text{N}^+\text{OH}^-$  as the active ingredient.

[0050] (b) The aqueous TMAH solution described in (a) additionally comprising a non-ionic surfactant of low foam type as long chain alcohol ethoxylates, ethoxylated alkyl phenols such as octylphenoxy polyoxyethanol, and ethylene oxide/propylene oxide block co-polymers, and glucose based alkyl polyethers or alkyl polyglycosides which to a large extent are biodegradable.

[0051] (c) An aqueous alkaline solution comprising tetramethyl ammonium hydroxide, 2-hydroxyethyl trimethyl ammonium hydroxide (Choline), tetraethyl ammonium hydroxide, and combinations thereof, at a concentration of less than 1 wt % additionally comprising an alkali metal hydroxide, for example potassium hydroxide, sodium hydroxide, and mixture thereof, and/or alkali-metal silicate, for example, sodium metasilicate, potassium metasilicate, sodium tripolyphosphate, and the like; and/or an alkanolamine, for example, 2-aminoethanol, at a concentration of less than about 1 wt %, the mixture may also contain a surfactant.

[0052] (d) The aqueous TMAH solution described in (a) additionally comprising between about 10 to about 30 vol. % of a high boiling and water soluble organic solvent, preferably dipropylene glycol monomethyl ether and/or tripropylene glycol monomethyl ether.

[0053] A representative process for mask cleaning according to this invention involves immersing the masks having paste residue, in an aqueous TMAH-based alkaline solution pre-heated at between about 130° F. to about 170° F. and ultrasonically agitating the same for between about 30 to about 60 seconds, rinsing immediately with water, preferably hot deionized water in an ultrasonic bath or using pressurized spray and drying with forced air, or  $\text{N}_2$ , preferably hot air or nitrogen. When using an ultrasonic or spray

rinse, rapid drying of the masks may be accomplished by a dip treatment or exposure to a fine mist of a lower boiling solvent, such as, isopropyl alcohol, or simply exposure to its vapor after the water rinse and then air dried.

[0054] The aqueous cleaning compositions described above which are comprised of a combination of TMAH and sodium hydroxide, potassium hydroxide and/or an organic amine have the advantage of reducing the TMAH concentration without affecting the cleaning performance. A similar reduction in TMAH concentration is obtained by adding between about 10 and about 30 vol % dipropylene glycol methyl ether (DPM) and/or tripropylene glycol methyl ether (TPM), and related water soluble high boiling organic solvents.

[0055] It has been found, unexpectedly, that the conductive metal from the removed paste essentially completely settles at the bottom of the ultrasonic tank and as such can be quantitatively recovered as a powdery material for recovery and reclamation.

[0056] An advantage of ultrasonic cleaning with these aqueous solutions is that a multiple number of masks can be arranged in a rack and cleaned simultaneously in the same bath solution which can be reused after filtering out the separated solids, thus providing material cost reduction, waste minimization, and the conservation of water. Similarly, screening accessories of all different sizes and shapes can be cleaned all together using an ultrasonic bath followed by a water rinse and a dry cycle.

[0057] According to this invention, an ultrasonic cleaning method is preferred when the cycle time requirement is not a factor, for example, in low volume production, and cleaning of screening accessories, such as, nozzles, squeegee blades, and paste residue removal from fragile stencil mask types where a pressure spray may cause damage to the mask integrity.

[0058] Major benefits of the aqueous cleaning method employing TMAH-based alkaline solutions include: no hazardous volatile emissions, no hazardous waste, no sludge treatment issues, low cleaner volume requirement, waste minimization, compatibility with cleaning accessories of all sizes and shapes, multiple mask cleaning with the same cleaning solution causing material cost reduction and minimizing water consumption.

[0059] It is preferred that the quaternary ammonium hydroxide is a tetraalkyl ammonium hydroxide selected from the group comprising tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, trimethyl-2-hydroxyethyl ammonium hydroxide (Choline), tetrabutyl ammonium hydroxide, and combinations thereof.

[0060] The preferred aqueous alkaline composition based on quaternary ammonium hydroxide is aqueous tetramethyl ammonium hydroxide (TMAH) having a concentration in the range of between about 0.5 to about 5.0 weight percent based on  $(\text{CH}_3)_4\text{N}^+\text{OH}^-$  solids dissolved in water, which may also contain a water soluble organic solvent.

[0061] However, the aqueous tetramethyl ammonium hydroxide (TMAH) solution could contain at least one non-ionic surfactant selected from the group comprising low foam long chain linear alcohol ethoxylates of the type poly(oxyethylene)dodecyl ether; ethoxylated alkyl phenols



of the type octylphenoxy-polyethoxy ethanol, nonylphenoxy poly(ethyleneoxy) ethanol, and the like; and polyoxyethylene-polyoxypropylene block co-polymers, poly(oxyethylene-oxypropylene)nonyl phenyl ether, poly(oxyethylene)dodecyl ether; and polyalkyl glycosides of the type glucose-decyl-octyl ether oligomers, and combinations thereof.

[0062] The aqueous TMAH solution could also contain at least one alkali metal hydroxide, selected from sodium hydroxide, potassium hydroxide, and/or alkali metal salt selected from sodium carbonate, potassium carbonate, sodium metasilicate, sodium tripolyphosphate, and combinations thereof.

[0063] The aqueous TMAH solution could also contain at least one aliphatic amine selected from the group comprising monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof. And, wherein the aliphatic amines could constitute between about 10 to about 30 percent of TMAH active ingredient concentration in deionized water to provide an aqueous cleaning solution with a pH in the range of between about 12.1 and about 13.1.

#### EXAMPLES

[0064] Various aspects of the present invention are further illustrated by referring to the following examples which are intended only to further illustrate the invention and are not intended to limit the scope of the invention in any manner.

##### Example 1

[0065] Molybdenum metal masks having fine etched features for via and wiring metallurgical patterns, and for I/O pads, suitable for multi-layer ceramic substrates were used for screening conductive pastes on ceramic green sheets with a screening tool. Various paste types screened on green sheets through metal masks are comprised of Mo, Cu, W, Ni as the metal component. The metal component was in the range of between about 60 to about 85 wt % as powder dispersed in between about 2 percent and 5 percent ethylcellulose or an alternative binder system such as polyhydrocarbon based thermoplastic polymer binder and a high boiling polar solvent of ester-alcohol type like 2,2,4-trimethylpentane diol 1,3-monoisobutyrate, glycol-ether type as diethylene glycol alkylether acetate, or a non-polar hydrocarbon oil.

[0066] Also included in the paste compositions are: thickening agents such as, for example, triglyceride fatty acid esters and dispersants/surfactants as alkyl sarcosinates, and other additives like antioxidants, coloring agents, corrosion inhibitors, etc. Paste compositions based on low molecular weight thermoplastic resins derived from petroleum hydrocarbons as the binder in conjunction with hydrocarbon oil as the solvent vehicle constituted lipophilic or non-polar paste types while the others are of polar type.

[0067] Some of the pastes tested contained an inorganic filler such as glass, ceramic, or glass frit in conjunction with a metal powder as the major component. After the paste screening operation, the masks carrying the paste residue on the surface, and in and around the etched features were cleaned with an aqueous tetramethyl ammonium hydroxide (TMAH)-based solution as described in the following sub-examples:

[0068] (a) Ultrasonic cleaning of paste residue with aqueous tetramethyl ammonium hydroxide (TMAH):

[0069] A 1.5 percent solution of TMAH was prepared by diluting about 300 cc of a 25 percent (wt. %) concentrate (based on  $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ ) to about 5,000 cc with deionized water. The solution was heated to between about 140 and about 160° F. in an ultrasonic bath operated at a frequency of about 40 kHz. Mo metal masks having paste residue from the screening of Mo pastes including both the polar and non-polar type pastes were immersed in the heated cleaning solution and ultrasonically agitated for about 60 seconds followed by an immediate pressure spray rinse with hot deionized water at between about 110 and about 130° F., and forced air dry. Microscopic inspection of the cleaned masks showed a complete removal of residue from all areas of the mask regardless of the paste type used for screening.

[0070] Similarly, Electroform masks (Ni plated on an etched Cu foil) carrying residue from screening Cu and W pastes were cleaned within about 45 second using 1.0 percent TMAH solution at between about 140 to about 160° F. with ultrasonic agitation to provide complete removal of any residue from active and non-active areas of the masks. Similar results were obtained in the case of emulsion mask cleaning.

[0071] (b) Mask cleaning with aqueous TMAH-soluble organic solvent blend:

[0072] About a 0.7 percent (wt. %) solution of TMAH [based on  $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ ] prepared by diluting a 25 percent TMAH concentrate with an 85:15 (volume ratio) blend of deionized water and dipropylene glycol monomethyl ether (DPM), respectively, was heated at between about 145 to about 160° F. in an ultrasonic bath operated at a frequency of about 40 kHz. Masks carrying paste residue from various types of pastes were stacked in a carrier and immersed in the heated aqueous cleaning solution, and ultrasonically agitated for between about 45 to about 60 seconds followed by an immediate spray rinse with deionized water and forced air dry. Microscopic examination of the masks after cleaning showed no evidence of residue on the surface or in the fine pitch etched features of the active area.

[0073] When 3-methoxy-1-butanol or tripropylene glycol monomethyl ether (TPM) were used as a replacement of DPM or in combination with it, equally effective cleaning was accomplished under the same cleaning conditions. These organic solvent modified aqueous TMAH-based cleaning solutions were found to be effective for both the polar and non-polar paste residue in addition to providing a somewhat enhanced cleaning efficiency relative to the unmodified solution.

[0074] These solutions have no foaming problem and therefore can also be used with pressurized spray cleaning of emulsion masks at low pressure, for example, in the range between about 50 and about 70 psi. Since the emulsion masks are relatively fragile, ultrasonic cleaning or low pressure spray cleaning is preferred.

[0075] (c) Aqueous TMAH-based/low foam surfactant containing solution:

[0076] About 1 percent (wt. %) TMAH in deionized water was prepared by diluting a 25 percent TMAH concentrate in water to which was added about 0.05 percent (wt. %) of a low foam non-ionic surfactant, octyl phenoxy-polyethoxy ethanol (70 percent active) formulation in polyethylene glycol and water. The resulting solution was heated to

between about 140 and about 170° F. in an ultrasonic bath and tested for mask cleaning using the process described in (a) above. It was found that the residue on metal masks and emulsion masks from the polar and non-polar pastes was effectively removed.

[0077] (d) Removal of paste residue on screening accessories:

[0078] Various forms of paste application equipment including disassembled nozzle components, and other paste handling items carrying dried paste residue were soaked in a heated aqueous TMAH-based/surfactant-containing solution described in (c) above, for between about 5 to about 10 min with ultrasonic off. The soak cycle was followed by ultrasonic agitation for between about 2 to about 3 min and an immediate water rinse, preferably deionized water, using an ultrasonic bath or a pressurized spray and a hot air dry, for example, using a dryer.

#### Example 2

[0079] The following aqueous alkaline solutions comprising TMAH and having pH of between about 11.9 to about 12.9 were used for low pressure spray cleaning and ultrasonic cleaning. After the cleaning step, the masks were immediately spray rinsed with hot water and blow dried using nitrogen. Again, a highly effective and efficient removal of paste residue from all types of pastes was obtained from all areas of the masks including the fine line feature region of the active area:

[0080] (a) An aqueous solution comprising a blend of TMAH, sodium hydroxide (NaOH) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) was prepared such that the total concentration of active ingredients obtained was about 1.1 wt. percent comprising 0.6:0.2:0.3 wt. ratio of TMAH:NaOH: $\text{Na}_2\text{CO}_3$ , respectively.

[0081] For mask cleaning, the solution was heated at between about 145 to about 155° F. and sprayed onto masks carrying residual paste from a prior screening pass, with a hand-held single nozzle set up at between about 60 to about 70 psi pressure for between about 35 to about 45 seconds followed by a spray rinse with deionized water at about 110° F., and blow dried using nitrogen. Microscopic inspection of the cleaned masks showed no evidence of residual paste on the mask. The same solution provided excellent cleaning with ultrasonic cleaning with the advantage that a much lower volume of cleaning solution was consumed due to the processing of multiple masks at one time and the repeated use of the same solution before it required replacing with a fresh solution.

[0082] (b) An aqueous solution comprising blend of TMAH and ethanolamine:

[0083] A cleaning solution was prepared having TMAH/ethanolamine with a total concentration of active ingredients of 1.1 percent and a relative ratio of about 9:2, respectively, for the two components. Mask cleaning with this solution using a pressurized spray and with ultrasonic agitation according to the process described above showed excellent cleaning of all types of pastes on all types of masks.

[0084] While the present invention has been particularly described, in conjunction with a specific preferred embodiment, it is evident that many alternatives, modifications and

variations will be apparent to those skilled in the art in light of the foregoing description. It is therefore contemplated that the appended claims will embrace any such alternatives, modifications and variations as falling within the true scope and spirit of the present invention.

What is claimed is:

1. A composition for removing at least a portion of screening paste residue from a paste screening object with at least one aqueous alkaline composition comprising at least one quaternary ammonium hydroxide as at least one component of said composition.

2. The composition of claim 1, wherein said screening paste comprises at least one metal and/or inorganic particulate material, at least one polymeric binder and at least one solvent vehicle having at least one surfactant/dispersant and at least one thickening agent as additives, and optionally containing at least one antioxidant and at least one corrosion inhibitor.

3. The composition of claim 1, wherein said screening object is selected from a group consisting of a screening mask, a screening fixture, paste making equipment and processing equipment.

4. The composition of claim 1, wherein said screening object is selected from a group consisting of a metallic mask and an emulsion mask on a metal mesh.

5. The composition of claim 4, wherein material for said metal mesh is stainless steel.

6. The composition of claim 1, wherein said quaternary ammonium hydroxide is a tetraalkyl ammonium hydroxide selected from the group consisting of tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide, trimethyl-2-hydroxyethyl ammonium hydroxide (Choline), tetrabutyl ammonium hydroxide, and combinations thereof.

7. The composition of claim 1, wherein said aqueous quaternary ammonium hydroxide is tetramethyl ammonium hydroxide.

8. The composition of claim 1, wherein said quaternary ammonium hydroxide component of said aqueous alkaline composition is aqueous tetramethyl ammonium hydroxide (TMAH) having concentration in the range of between about 0.5 to about 5.0 weight percent based on  $(\text{CH}_3)_4\text{N}^+\text{OH}^-$  solids dissolved in water.

9. The composition of claim 8, wherein said aqueous alkaline composition containing tetramethyl ammonium hydroxide (TMAH) also contains at least one non-ionic surfactant selected from the group consisting of low foam long chain linear alcohol ethoxylates of the type poly(oxyethylene)dodecyl ether; ethoxylated alkyl phenols of the type octylphenoxy-polyethoxy ethanol, nonylphenoxy poly(ethyleneoxy) ethanol, and the like; and polyoxyethylene-polyoxypropylene block co-polymers, poly(oxyethylene-oxypropylene)nonyl phenyl ether, poly(oxyethylene)dodecyl ether; and polyalkyl glycosides of the type glucose-decyl-octyl ether oligomers, and combination thereof.

10. The composition of claim 8, wherein said aqueous alkaline composition containing TMAH also contains between about 10 to about 30 volume percent of at least one high boiling water soluble organic solvent selected from the group consisting of benzyl alcohol, dipropylene glycol alkyl ethers, tripropylene glycol alkyl ethers, 3-methoxy-1-butanol, methoxy propanol, and mixtures thereof, and wherein said alkyl is selected from a group consisting of butyl, ethyl,

methyl and propyl group, or said alkyl is a hydrocarbon radical selected from the group consisting of  $C_nH_{2n+1}$ , where  $n=1-4$ .

11. The composition of claim 8, wherein said aqueous alkaline composition containing TMAH also contains at least one alkali metal hydroxide and/or at least one carbonate and/or at least one alkali metal silicate selected from a group consisting of sodium hydroxide, potassium hydroxide, and mixtures thereof, and/or sodium carbonate, sodium sesquicarbonate, sodium metasilicate, potassium metasilicate, sodium tripolyphosphate, and mixtures thereof.

12. The composition of claim 8, where said aqueous alkaline composition containing TMAH contains at least one aliphatic amine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof.

13. The composition of claim 12, wherein said aliphatic amines constitute between about 10 to about 30 weight percent of TMAH active ingredient concentration in deionized water to provide aqueous cleaning solution.

14. The composition of claim 1, wherein said composition of removing screening paste residue from a paste screening object with aqueous alkaline composition comprising quaternary ammonium hydroxide as at least one component of said composition, comprises the steps of:

- (a) immersing said screening object in at least one pre-heated cleaning solution at between about 130° F. to about 170° F. in an ultrasonic bath and subjecting to ultrasonic agitation in said pre-heated cleaning solution for between about 30 seconds and about 2 minutes,
- (b) removing said screening object from said cleaning solution and immediately subjecting said screening object to at least one ultrasonic or spray rinse with water.

15. The composition of claim 14, wherein said water is preferably deionized water.

16. The composition of claim 14, wherein after step (b) said screening object is dried using air and/or nitrogen.

17. A cleaning apparatus comprising:

- (a) at least one means for immersing at least one screening object having screening paste residue on said screening object in at least one container;
- (b) wherein said container comprises at least one aqueous alkaline composition having at least one quaternary ammonium hydroxide as at least one component of said composition;
- (c) wherein said aqueous alkaline composition is subjected to at least one means of mechanical agitation;
- (d) said at least one means of mechanical agitation also causes separation of at least a portion of said paste residue from said screening object; and
- (e) at least one means of rinsing said screening object with water after cleaning with said aqueous alkaline solution, followed by at least one means of drying said screening object after said cleaning and rinsing operation.

18. A cleaning apparatus comprising:

- (a) at least one means for pressure spraying at least one solution onto at least one screening object having screening paste residue on said screening object; and
- (b) wherein said at least one solution comprises at least one aqueous alkaline composition having at least one quaternary ammonium hydroxide as at least one component of said composition.

\* \* \* \* \*



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(54) **SEMI-AQUEOUS SOLVENT CLEANING OF PASTE PROCESSING RESIDUE FROM SUBSTRATES**

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(58) **Field of Search** ..... 134/60, 76, 184, 134/111, 2, 1, 22.1, 22.14, 22.19, 36, 40, 42, 902; 510/175, 407, 413, 421

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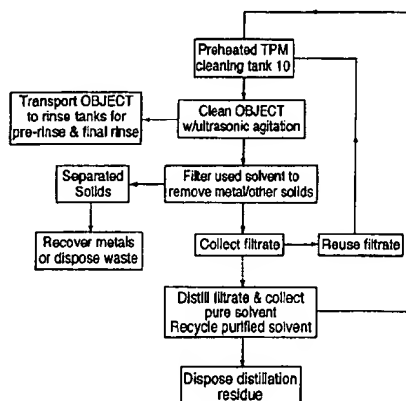
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(57) **ABSTRACT**

A process of cleaning of objects that relate to semiconductor fabrication processes, such as, for example, conductive paste screening in the production of multilayer ceramic substrates and composite solder paste by stencil printing in electronic circuit assembly. Specifically, the process removes a metal/polymer composite paste from screening masks and associated paste making and processing equipment used in printing conductive metal pattern onto ceramic green sheet in the fabrication of semiconductor packaging substrates. The process also cleans solder paste residue from stencil printing equipment used in electronic module assembly surface mount technology for SMT discretes, solder column attachment, and BGA (Ball Grid Array) attachment on ceramic chip carrier or for screening solder paste onto printed circuit board. More particularly, paste residue is cleaned from metal, ceramic, and plastic substrates by a non-alkaline semi-aqueous cleaning method employing high boiling propylene glycol alkyl ether or mixtures of propylene glycol alkyl ether and propylene glycol solvents.

20 Claims, 4 Drawing Sheets



Semi-Aqueous Solvent Cleaning with TPM

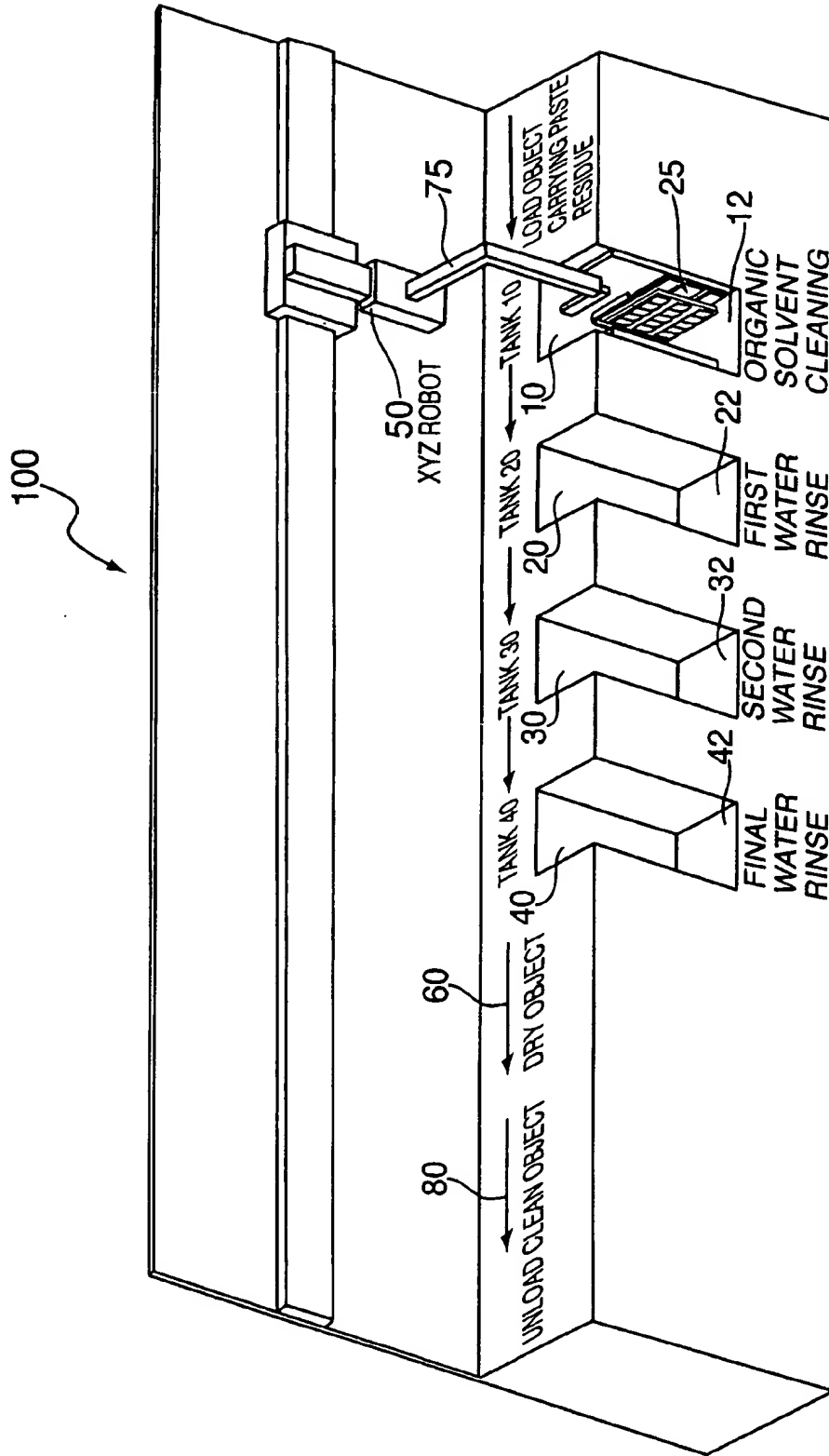


FIG. 1

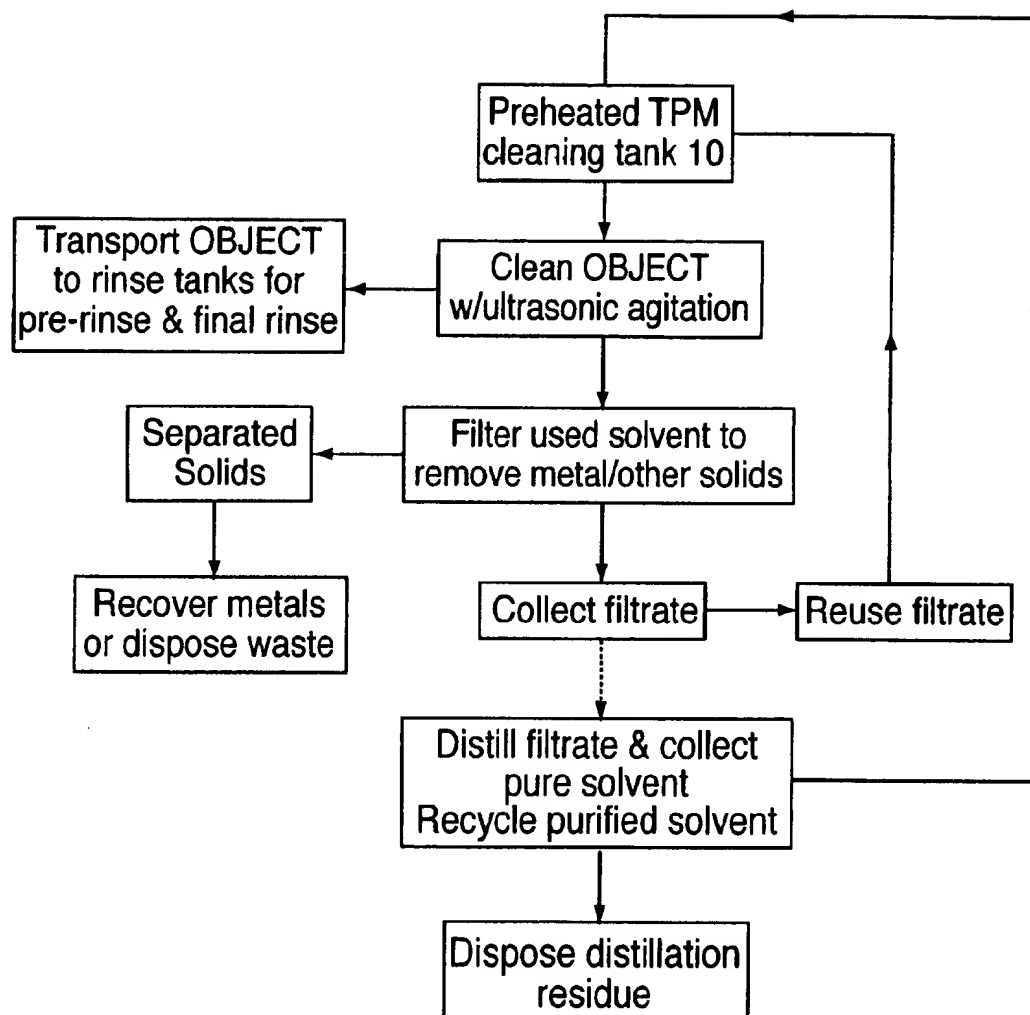
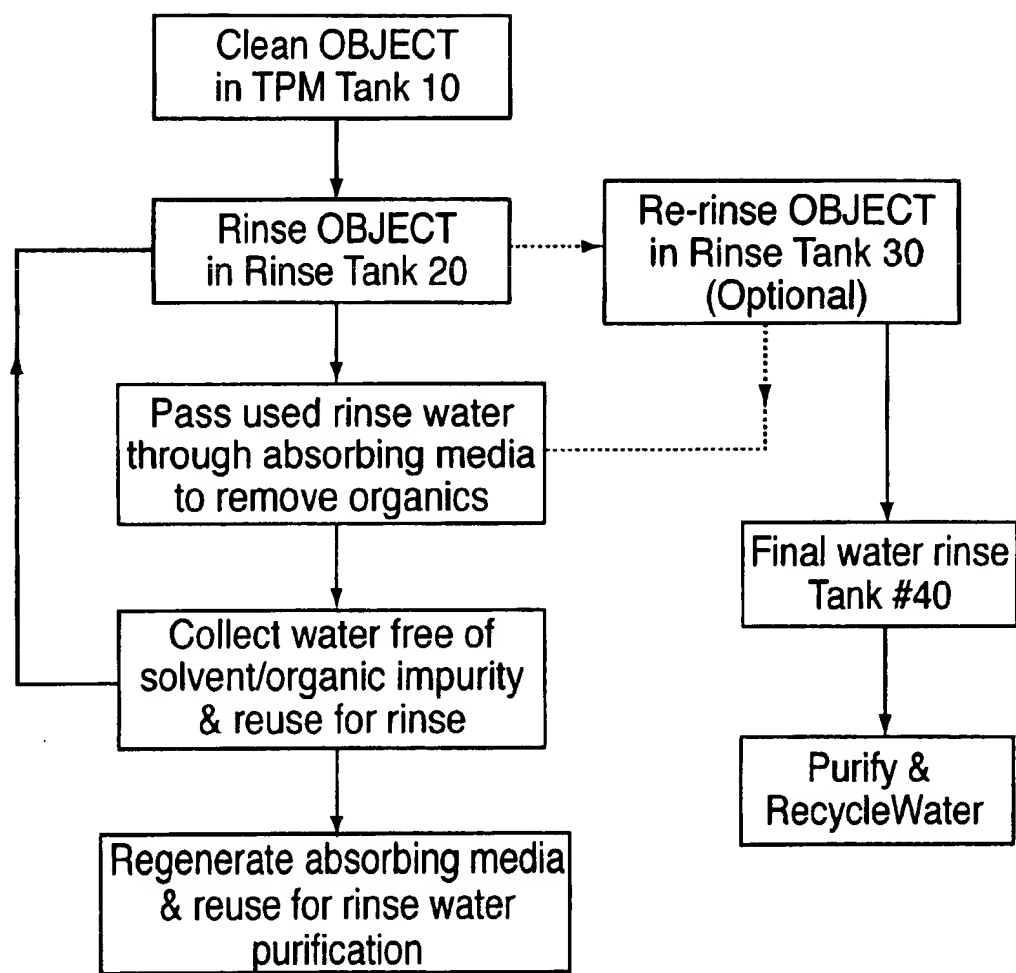
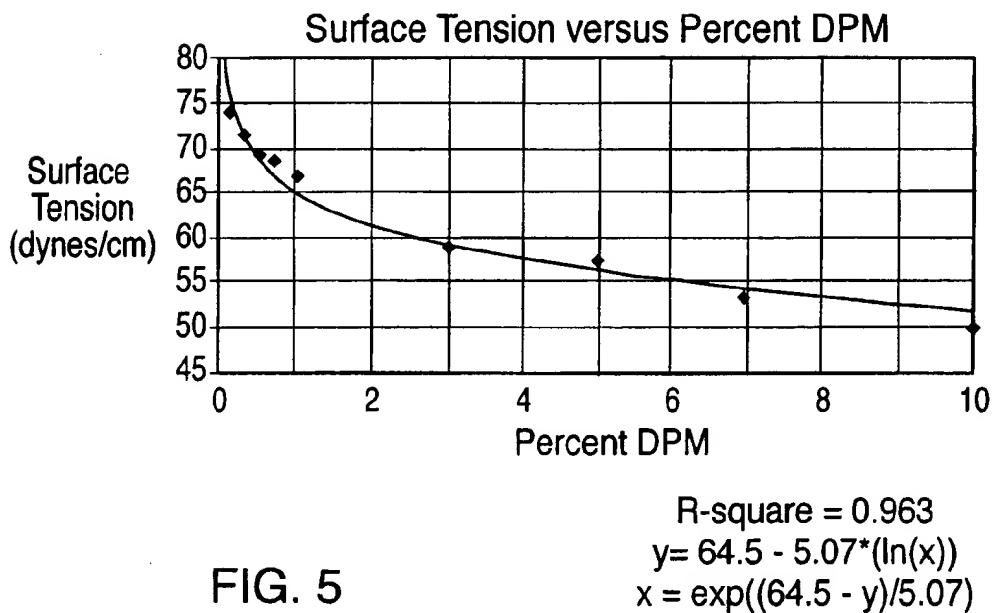
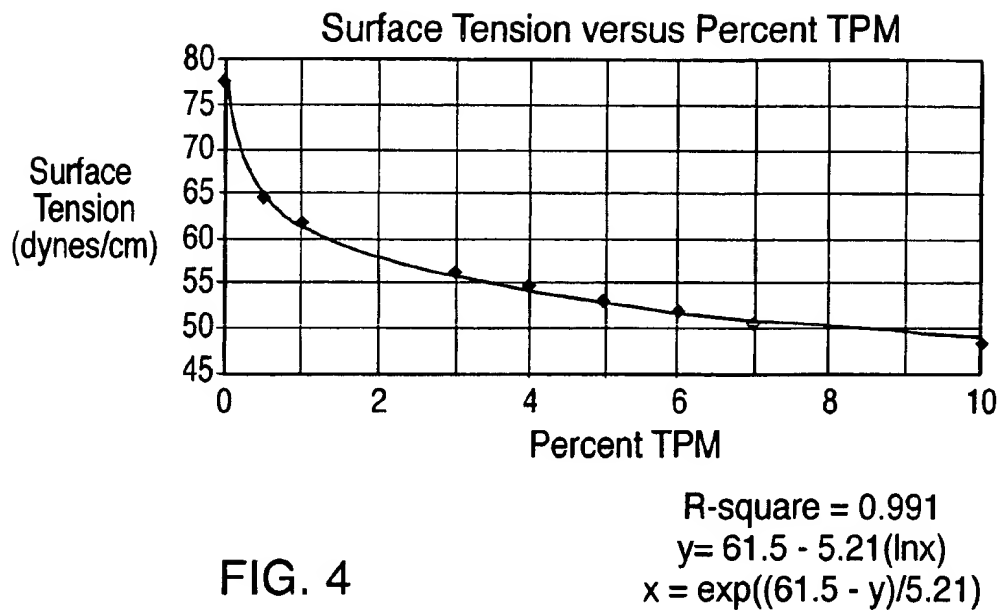


FIG. 2

Semi-Aqueous Solvent Cleaning with TPM

**FIG. 3**

Semi-Aqueous Solvent Cleaning with TPM  
Reuse of Rinse Water





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# SEMI-AQUEOUS SOLVENT CLEANING OF PASTE PROCESSING RESIDUE FROM SUBSTRATES

## FIELD OF THE INVENTION

The present invention relates generally to a new apparatus and method of semi-aqueous solvent cleaning of paste processing residue from substrates. More particularly, the invention encompasses an apparatus and a method that utilizes a semi-aqueous solvent cleaning method for cleaning of paste residue from screening objects comprising the use of at least one propylene-glycol alkyl-ether solvent.

## BACKGROUND OF THE INVENTION

In the fabrication of multilayer ceramic (MLC) substrates for packaging semiconductor devices, conductive metal patterns are screened onto individual ceramic green sheets by printing, such as, extrusion printing, which uses metal mask, such as, Mo, Ni, or Cu, which are placed in contact with the green sheet, or by screen printing, which involves paste squeegee using mesh mask or emulsion mask. After screening, the green sheets are assembled and aligned, and laminated, followed by sintering operation to form multilayer ceramic substrate having internal metallurgy for mounting and interconnecting a plurality of integrated circuit semiconductor devices.

For advanced ground rule electronic packaging structures requiring to print closely spaced conductive metal patterns on a substrate, the screening masks used have highly dense fine dimension etched features. Under certain conditions such screening masks may have the problem of paste residue entrapment in the mask features in addition to a surface residue when the paste is screened to deposit conductive pattern on green sheets. This requires that the metal mask be cleaned after one or more screening passes to eliminate/minimize the possibility of defects in a subsequently screened pattern. Any defects in the screened paste pattern replicates into the final product causing yield loss.

Conductive pastes used in screening processes for delineation of wiring and/or via metallurgy, and I/O pad (input-output) patterns comprise metal particles dispersed in an organic binder and solvent vehicle along with wetting agents, dispersants/surfactants, plasticizers, and other additives, such as, thickening agents, antioxidants, and coloring agents which are all well known in the fabrication of electronic components.

Most commonly used conductive pastes in multilayer ceramic fabrication are based on molybdenum or tungsten metal powder dispersed in an organic polymer binder, such as, for example, ethyl cellulose, polymethyl methacrylate, and the like, or poly-hydrocarbon based thermoplastic resins dissolved in a high boiling solvent system.

Conductive pastes that are typically used for screening processes in multilayer ceramic comprise molybdenum, copper, tungsten, nickel, gold, tin, and the like. Because of the variety and complex chemical make-up of metal/polymer composite pastes, it is required that the mask cleaning medium and process selected be such that it provides complete and efficient cleaning of all types of pastes from screening masks and associated equipment, such as, extrusion heads or paste nozzles, etc.

Solder pastes commonly used in electronic assembly processes for interconnections constitute eutectic alloys, specifically, Pb—Sn, Bi—Sn, In—Sn, and related powder

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alloys dispersed in an organic carrier. Solder paste application onto substrates for component attachment is done by screen printing through a screen stencil, for example, stainless steel stencil, or by the dispense method. Various solder paste formulations constitute a eutectic alloy dispersed in an organic carrier, for example, a solvent, rheology modifier, fluxing agent, such as, rosin based flux. It is important to clean solder paste residue from metal mask stencils, especially in the case of ultra-fine pitch BGA (Ball Grid Array) attachment to assure defect-free printing on substrate metal pads and thus eliminate solder defects.

Traditionally used cleaning solvents for cleaning/degreasing purposes in many industrial and consumer product applications include aromatic hydrocarbons, chlorinated solvents, typically, 1,1,2-trichloroethylene, perchloroethylene, methylene chloride, and fluorochlorocarbons as CFC-113, and CFC-112. The chlorinated solvents were especially preferred because they are non-flammable, i.e., have no flash point, and are highly effective solvents.

Because of the environmental and health issues associated with the use halogenated hydrocarbon solvents in production processes, there has been major focus in the past decade to introduce environmentally safer/acceptable organic solvent alternatives, and water-based cleaning formulations. Recently, ultrasonic and spray cleaning equipment for water-based cleaning chemistry have become commercially available and several detergent compositions have been described in the patent literature for cleaning/degreasing purposes. These compositions are used, for example, for cleaning printed circuit board assemblies and other parts in device fabrication to remove soldering flux, oil/grease, and other organic residues invariably formed during bonding and assembly processes in microelectronics. These compositions are generally based on a combination of surfactants in water and/or alkaline detergent compositions, comprising alkali metal salts, such as, sodium metasilicate, sodium carbonate, tribasic sodium phosphate, sodium tripolyphosphate, and combinations thereof, as well as, highly alkaline solutions based on alkali metal salts, alkali metal hydroxides, and mixture thereof with alkanolamines. Aqueous cleaner formulations comprising this category of alkali metal carbonate and bicarbonate salts are utilized with an alkali metal silicate, as described in U.S. Pat. No. 5,234,506 (Winston), for the removal of solder flux, oils, waxes, and greasy substances, adhesives and other residues from electronic circuit assemblies, such as, printed circuit or printed wiring boards during their fabrication.

Alternate organic solvent cleaning methods are based on the use of low boiling alcohol, ketone, or ester solvents, for example, isopropyl alcohol (IPA), acetone, n-butylacetate, methyl ethyl ketone (MEK), and aromatic hydrocarbons, specifically xylene. These solvents have safety and environmental issues due to their low boiling points, high flammability, volatile emissions and VOC (Volatile Organic Compound) regulations, and thus are considered undesirable for production processes. Various aqueous cleaning alternatives designed for saponification mechanism, on the other hand, generally have a high pH (>11–13) detergent formulations. High pH aqueous cleaners have associated safety issues which require special handling and costly equipment designs to assure protection against any accidental contact exposure. With alkaline aqueous cleaners comprising alkali metal salts, for example, phosphates, silicates, hydroxides, and surface active agents, there is also an issue of wastewater management for compliance with the Clean Water Act regulations which require that all possible sources of aquatic toxicity and other envi-

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ronmentally undesirable constituents be removed from the effluent before discharge to surface waters. This requires special and costly wastewater treatments involving precipitation with complexing agents to form sludge that carries active ingredients of cleaning compositions, metals, and other dissolved constituents resulting in solids loading to the waste. To minimize waste and reduce cost with conservation of water in aqueous cleaning, there is currently significant industry direction toward environmentally suitable zero waste processes by devising methodology for reclamation, recycling, and reuse.

### PURPOSES AND SUMMARY OF THE INVENTION

The invention is a novel method and an apparatus for semi-aqueous solvent cleaning of paste processing residue from substrates.

This invention basically is a semi-aqueous method of cleaning polymer/metal composite paste residue from screening masks/stencils and paste processing equipment in the production of multilayer ceramic substrates, organic chip carriers and cards, and of composite solder paste application in electronic circuit assembly. The method according to this invention involves a cleaning cycle using a high boiling, low vapor pressure, and substantially water soluble solvent, specifically, a propylene-glycol alkyl-ether solvent followed by a first water rinse to remove the cleaning solvent carry-over on the substrate from the cleaning tank, a second water dip/rinse (optional) to remove last traces of organic contaminants, if any, and then a final thorough water rinse and drying operation.

Therefore, one purpose of this invention is to provide an apparatus and a method that will help clean polymer/metal composite paste residue from a substrate.

Another purpose of this invention is to provide for a non-hazardous, low cost, cleaning option for paste residue from substrates.

Still another purpose of this invention is to have a semi-aqueous cleaning method for removing paste screening residue from screening equipment.

Yet another purpose of this invention is to provide a non-alkaline semi-aqueous water-based cleaning method for paste screening and paste processing equipment as a superior alternative to chlorinated solvents, volatile organic solvents and alkaline aqueous cleaning compositions in multilayer ceramic manufacturing and in microelectronic assembly processes.

Another purpose of this invention is to provide a semi-aqueous cleaning method for cleaning screens/stencils and paste processing parts by using high boiling propylene-glycol alkyl-ether solvents as a replacement of volatile organic solvents and aqueous alkaline cleaning to eliminate chemical safety concerns, volatile emissions and hazardous waste.

Yet another purpose of this invention is to provide a method for cleaning of paste residue from substrates using a high boiling organic solvent for the cleaning solvent without adding water or other additives such as surface active agents or other adjuvants such that the solvent can be easily recovered and recycled.

Still another purpose of this invention is to provide a semi-aqueous alternative to flammable solvents and aqueous alkaline cleaning compositions in cleaning screening paste residue and solder paste residue from substrates in micro-electronic fabrication using a propylene-glycol alkyl-ether

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solvent that is effective in removing polar, non-polar, or hydrophilic and hydrophobic paste residue from metal and plastic surfaces.

It is also the purpose of this invention to provide a solvent-based semi-aqueous cleaning method for screening masks/stencils and paste processing equipment which does not require special wastewater treatment.

Yet another purpose of this invention is to provide a semi-aqueous cleaning method for paste screening masks which allows easy removal of washed-off metal by filtration and solvent recovery, for example, by distillation from the waste liquid and provides benefit of waste minimization.

Still another purpose of this invention is to provide a semi-aqueous cleaning method using a high boiling propylene-glycol alkyl-ether solvent that is compatible with metal masks, emulsion masks, electronic components and polymer adhesives used in assembly processes, and all contacting materials in the cleaning equipment.

Still yet another purpose of this invention is to provide a semi-aqueous cleaning method with an organic solvent which is non-flammable high boiling Class-III combustible, (flash point of greater than about 140° F.), preferably Class-IIIB combustible, (flash point of greater than about 200° F.), non-corrosive, and has no contact hazard concerns.

Therefore, the inventors are disclosing a first invention which comprises a semi-aqueous solvent cleaning method for cleaning of paste residue from at least one object comprising the use of at least one propylene-glycol alkyl-ether solvent.

The inventors are disclosing a second invention which comprises a method for cleaning paste residue from at least one object, comprising the steps of:

(a) Pre-heating propylene-glycol alkyl-ether solvent in a tank having at least one ultrasonic bath at between about 45 to about 80° C.,

(b) Immersing said paste residue carrying object in said preheated solvent and subjecting said object to ultrasonic agitation for between about 1 to about 10 min, and

(c) Transferring said object to a tank having preheated water at between about 45 to about 70° C., and subjecting said object to at least one immersion spray and/or ultrasonic agitation, and thereby cleaning said paste residue from said at least one object.

The inventors are disclosing a third invention which comprises an apparatus for cleaning paste residue from at least one object, comprising:

(a) at least one tank containing at least one pre-heated propylene-glycol alkyl-ether solvent in said tank, wherein temperature of said solvent in said is between about 45 to about 80° C., and wherein said tank further having at least one ultrasonic agitator,

(b) at least one means for immersing said paste residue carrying object in said pre-heated solvent and subjecting said object to ultrasonic agitation for between about to about 10 min, and

(c) at least one means for transferring said object to a tank having preheated water at between about 45 to about 70° C., and subjecting said object to at least one immersion spray and/or ultrasonic agitation, and thereby cleaning said paste residue from said at least one object.

### BRIEF DESCRIPTION OF THE DRAWINGS

The features of the invention believed to be novel and the elements characteristic of the invention are set forth with

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particularity in the appended claims. The drawings are for illustration purposes only and are not drawn to, scale. Furthermore, like numbers represent like features in the drawings. The invention itself, however, both as to organization and method of operation, may best be understood by reference to the detailed description which follows taken in conjunction with the accompanying drawings in which:

FIG. 1, is a representative drawing showing the apparatus assembly for the semi-aqueous cleaning process using this invention.

FIG. 2, is a block diagram showing one preferred mode of carrying out this invention.

FIG. 3, is a block diagram showing another preferred mode of carrying out this invention.

FIGS. 4 and 5, illustrate the calibration data in Tables 1 and 2, respectively, with graphical representation.

#### DETAILED DESCRIPTION OF THE INVENTION

This invention relates to cleaning of objects that relate to semiconductor fabrication processes, such as, for example, conductive paste screening in the production of multilayer ceramic substrates or organic chip carriers and cards, and composite solder paste by stencil printing in electronic circuit assembly. This invention is concerned with removing, for example, a metal/polymer composite paste from screening masks and associated paste making and processing equipment used in printing conductive metal pattern onto ceramic green sheets in the fabrication of semiconductor packaging substrates. This invention is also concerned with the cleaning of solder paste from stencil printing equipment used in electronic module assembly, for example, in surface mount technology for SMT discretes as capacitors and resistors joining on chip carrier, solder column attachment, and BGA (Ball Grid Array) attachment on ceramic chip carrier or for screening solder paste onto printed circuit board. More particularly, this invention is concerned with cleaning of paste residue from metal, ceramic, and plastic substrates by a non-alkaline semi-aqueous cleaning method employing high boiling solvents which are partially or completely water soluble, particularly, propylene glycol alkyl ether solvents and thus can be rinsed off with water following the cleaning cycle.

Manufacture of semiconductor packaging products, such as, multilayer ceramic (MLC) substrates, typically employs the technique of conductive pattern screening on ceramic green sheet through a stencil mask using a variety of polymer-metal composite pastes to delineate a conductive pattern for the desired circuitry. In this process, some paste residue is left behind on the surface and inside the fine etched features of the mask. The residue entrapped in the mask features, and on the surface of the mask must be removed before the mask can be reused. This involves cleaning after one or more screening passes, depending on whether the paste is fast drying or slow drying, otherwise the paste residue can cause defects in a subsequently screened conductive pattern. A particular combination of a polar and/or non-polar polymer binder and solvent vehicle system selected for dispersing metal filler determines the solubility and wettability characteristics of the resulting paste which may range from hydrophilic to highly hydrophobic and which may be fast drying or slow drying.

Selection of conductive screening pastes that are based on a variety of polymer binder-solvent vehicle systems is dictated by several considerations, viz, requirement for a particular circuit pattern, drying characteristics of the paste,

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match of paste shrinkage with that of ceramic, and overall compatibility of the paste with green sheet materials for the necessary wettability and adhesion.

The screening masks used in the semiconductor industry are typically made of metal, such as, etched Mo mask, Cu/Ni electroform mask and emulsion masks for silk screening, such as, for example, stainless steel mesh with at least one photoresist coating of a suitable emulsion, such as, the polyacrylic-polyester based emulsion coatings.

The present invention provides a semi-aqueous cleaning method for mask cleaning with high boiling and partially or completely water soluble organic solvent, preferably, tripropyleneglycol methyl ether (TPM), as an environmentally safer, non-corrosive, and non-hazardous alternative to chlorinated solvents and flammable solvents, and high pH aqueous cleaners for effective cleaning of polymer/metal composite paste residue from screening equipment used in multilayer ceramic manufacturing, and solder paste residue on applicators used in component attachment for electronic circuit assembly.

The semi-aqueous cleaning method disclosed here employs completely or partially water soluble propylene-glycol alkyl-ethers, preferably without additives. This also has the special advantage of providing a non-corrosive, non-flammable and non-volatile solvent cleaning. Furthermore, the solvent, the rinse water, and the paste solids can easily be recovered and recycled, thus minimizing waste, reducing water consumption, eliminating the need for costly waste treatment, and providing an environmentally favorable industrial cleaning option and overall reduction in cost and waste.

Now referring to the figures, FIG. 1, illustrates the schematics of the cleaning apparatus assembly 100, and the sequence of process steps for practicing this invention. The cleaning apparatus assembly 100, basically comprises of at least one XYZ robot 50, having at least one robotic arm 75. The robotic arm 75, picks-up the object 25, to be cleaned from a loading area and moves it initially into a tank 10, having an organic cleaning solvent 12, of this invention. One could also have a plurality of cleaning tanks, e.g., tanks 20, 30, 40, containing cleaning fluids 22, 32, 42, respectively. The cleaning apparatus assembly 100, can also have a drying station 60, and an unload station 80, to unload the cleaned object 25, from the robotic arm 75.

After the robotic arm 75, picks-up the object 25, to be cleaned, such as, a substrate 25, having paste residue, the substrate 25, carrying paste residue is immersed in tank 10, which contains the cleaning solvent 12, preferably a dipropylene glycol methyl ether 12, or tripropylene glycol methyl ether 12, or a mixture thereof 12, which has been pre-heated at between about 45 to about 80° C., preferably, between about 50 to about 70° C., and equipped with ultrasonic or immersion spray or combination of ultrasonic and spray modes of agitation. The paste residue from the substrate 25, is removed by agitation in the solvent 12, for a predetermined time, preferably between about 1 to about 10 min, depending on the paste chemistry and the extent of residue deposit. The substrate 25, is then transferred to the tank 20, which contains water 22, preferably deionized water 22, and which is preferably preheated at between about 45 to about 70° C., to substantially remove the solvent carry-over from the cleaning tank (tank 10). The substrate 25, is then transported to tank 30, contains water 32, for a second (optional) water rinse to remove last traces of the organic solvent. The substrate 25, can then be subjected to a final thorough water rinse in tank 40, where the rinse water 42,

can be drain discharged or recycled, as it is essentially free of any organic or inorganic contaminants. The cleaned and rinsed substrate 25, is finally dried at station 60, for example, by forced hot air or N<sub>2</sub>, and unloaded at station 80, for further processing.

FIG. 2, is a block diagram showing one preferred mode of carrying out this invention. In this embodiment of the invention, as illustrated in FIG. 2, the used solvent after cleaning paste residue from a single or multiple substrates, sequentially or in parallel with a di- or tri-propylene glycol alkyl ether, is filtered or centrifuged to remove washed-off paste solids which include metals, inorganics, and insoluble organic solvents. The filtrate can be reused for cleaning paste residue till the cleaning effectiveness remains essentially unaffected, and it is replaced with fresh solvent when the cleaning performance degrades. The solvent can also be recovered/reclaimed from the solids-free filtrate by distillation and the recovered pure solvent can be reused/recycled. However, the distillation residue can be disposed-off as waste. The metal solids collected by filtration or centrifugation can also be reclaimed by commonly known methods or these can be disposed off.

The first water rinse (tank 20) can be used multiple times during which the carry-over solvent continues to build up, the relative concentration of carried-over solvent in water is monitored by periodic measurement of surface tension. The same rinse bath can be continued to be used until its surface tension reaches about 50 dynes/cm which corresponds to about 7% tri-propylene-glycol methyl-ether (TPM) in water.

Table 1, shows the data for measured surface tension at known concentration for correlation of TPM concentration in water with surface tension of the mixture, and Table 2, shows similar correlation of DPM concentration in water with surface tension. FIGS. 4 and 5, are graphical representation of the data given in Tables 1 and 2, respectively. A second water rinse can optionally included to remove last traces of organic solvent, and finally the final thorough water rinse (tank 40) and hot air or N<sub>2</sub> dry. The final rinse water is essentially free of organic or inorganic impurities and thus can be drain discharged or can be reused as it would require no prior treatment.

FIG. 3, illustrates a block diagram showing another preferred mode of carrying out this invention. This mode of practicing the invention provides reduction in waste, reduced solvent consumption, reduced water consumption, and reduced material cost.

The first water rinse (tank 20) containing dissolved solvent due to solvent carry-over from tank 10, can also be gotten rid of organics by passing through an absorbing medium, for example, activated charcoal bed to remove organics and reused, or it can be separately disposed off in compliance with the wastewater disposal regulations for organic solvent contaminated water. This mode of practicing the invention has the benefit of further reducing waste and reducing material and process cost.

The primary application for this invention would be in the removal of paste residue from screening masks/stencils and ancillary equipment used in screening conductive paste patterns on ceramic green sheets in the manufacture of multilayer ceramic substrates and in cleaning solder paste applicators in electronic component assembly processes. This invention is particularly concerned with removing polymer/metal composite paste residue from paste screening or paste dispensing equipment using high boiling organic solvent, particularly, propylene glycol alkyl ethers, for example, tripropyleneglycol monomethylether (TPM),

dipropyleneglycol monomethylether (DPM), and mixture thereof, and related materials to provide an environmentally favorable alternative to chlorinated solvents, and flammable solvents, and high pH aqueous alkaline cleaners.

Unlike high pH aqueous cleaning compositions, the semi-aqueous cleaning method according to this invention has no problem of corrosivity and contact hazard issues, and provides option for recovery and recycle of solvent as well as rinse water which can be reused. Semi-aqueous cleaning method using high boiling, partially or completely water soluble propylene-glycol alkyl-ether solvents according to this invention provides unique advantages of efficient removal of paste residue from metal and plastic substrates. This also allows easy recovery and recycling of the cleaning solvent and of rinse water, as well as reclamation of paste metals.

Basically, one could utilize any commercial cleaning equipment to carry out this invention. However, it is preferred that the equipment has ultrasonic cleaners with stainless steel tanks equipped with ultrasonic having frequencies between about 20 to about 40 kHz, and immersion spray modes with multi-tanks for separate cleaning, rinsing and drying steps. It is preferred that the equipment be equipped with re-circulation pumps, filter for continuous or intermittent removal of particulate, and ultra-filtration unit to allow reuse of the cleaning solvent, as well as, a water treatment systems, such that both the cleaning medium and the rinse water can be recycled.

This invention also provides an improved method to remove conductive paste residue from screening equipment in the production of multilayer ceramic (MLC), and solder paste applicators used in component attachment/interconnections for module assembly. The screening pastes used in MLC for defining via and wiring metallurgy pattern on ceramic green sheet and are comprised of metal filler of the type, molybdenum, copper, tungsten, nickel, gold, silver, some of which may also contain inorganic fillers as glass, ceramic powder, or glass frit, dispersed in an organic polymer binder and a high boiling organic solvent vehicle along with other necessary additives which include surfactants/dispersants, coloring agents, thickening agents or rheology modifiers, and antioxidants etc. Representative polymer binder systems in conductive paste formulations for multilayer ceramic include: cellulosic polymers such as ethyl cellulose, cellulose acetate butyrate, alkyl methacrylate polymers such as poly(methyl methacrylate), poly(ethyl methacrylate), hydrocarbon polymers based thermoplastic resins which are all hydrophobic, or the binder can be hydrophilic such as hydroxy ethyl cellulose, hydroxypropyl cellulose, hydroxymethyl cellulose, and the like.

High boiling solvent vehicles having low evaporation rates that are preferred for polymer/filler conductive paste dispersions include ester-alcohol or glycol-ether type solvents such as 2,2,4-trimethylpentane diol, 1,3, monoisobutylate (Texanol), diethylene glycol monomethylether acetate, diethylene glycol monobutylether acetate or butyl carbitol acetate (BCA), and the like. Generally, the solid component in screenable pastes comprises 70-85 percent (wt. %) metal filler, 1-5 percent of organic polymer binder and other organic additives, and the balance constituting the solvent vehicle system. Depending on a particular binder-solvent system used in paste formulation, the paste can be polar or non-polar, hydrophilic or oleophilic, having differences in affinity and adhesive characteristics for the mask surface in addition to having differences in drying rate.

According to this invention, it has been found that polymer/metal composite paste residue left on screening

masks and paste making and dispensing equipment in the process of conductive pattern screening on green sheet can be readily removed with partially or completely water soluble di- or tri-propylene-glycol alkyl-ethers by ultrasonic agitation at between about 45 to about 70° C., followed by a first water rinse to remove the carried-over solvent, an optional second water rinse, and the final water rinse, and finally drying the cleaned substrate according to the standard practice. The first water rinse can be simply a brief dip, during which the solvent displacement by water can be aided by mechanical agitation, for example, stirring, ultrasonic agitation, or spray. A similar method of cleaning is found effective for removing solder paste residue from paste applicators in component attachment in circuit assembly, for example, stainless steel stencils and dispensing equipment. In one embodiment of this invention, Mo metal masks or metal electroform masks, carrying conductive paste residue from a screening pass are submerged in an ultrasonic bath containing tripropylene glycol methyl ether (TPM) at between about 50 to about 70° C., and ultrasonics turned-on for between about 1 to about 5 min., when the residue is essentially completely washed off from the mask surface as well as from the fine etched features.

Subsequent to paste removal with TPM, masks are raised above the liquid to allow solvent drip for a few seconds, and then immediately transferred to the adjacent water rinse tank, preferably equipped for some form of agitation for few seconds, then an optional second water rinse for a few seconds to remove any residual solvent, followed by the final spray or ultrasonic rinse with copious amount of water and finally drying with forced air, preferably hot air or N<sub>2</sub>. In another embodiment of this invention, paste residue from screening and paste application equipment can be removed by spray cleaning using single nozzle or multi-nozzle spray gun but the ultrasonic cleaning is a preferred mode of cleaning with according to this invention due to solvent mist issues with organic solvent spray mode. The semi-aqueous method of cleaning disclosed herein effectively and efficiently removes all types of paste residues that may include polar, non-polar, hydrophilic, and hydrophobic type of screening and solder pastes from masks/stencils, typically Mo metal masks, metal electroform masks, stainless steel screens, and emulsion masks, solder paste applicators, which is free of environmental and safety issues, with no problem of metal corrosion, contact hazard, and flammability.

Representative candidates in propylene-glycol alkyl-ether category that can be used in the semi-aqueous cleaning method according to this invention are illustrated by the following chemistry:



where:

- R=CH<sub>3</sub>, n=2: Dipropylene glycol methylether (DPM),
- R=CH<sub>3</sub>, n=3: Tripropylene glycol methylether (TPM),
- R=C<sub>2</sub>H<sub>5</sub>, n=2 or 3: Di- or Tripropylene glycol ethylether,
- R=C<sub>3</sub>H<sub>7</sub>, n=2 or 3: Di- or Tripropylene glycol isopropylether,
- R=C<sub>4</sub>H<sub>9</sub>, n=2: Dipropylene glycol n-butylether (DPnB),
- R=C<sub>4</sub>H<sub>9</sub>, n=3: Tripropylene glycol n-butylether (TPnB),
- R=Methyl, n=x: Polypropylene glycol methylether (PPM), and
- R=n-Butyl, n=x: Polypropylene glycol butylether.

These can be used as single solvents, solvent blends with propylene-glycol alkyl-ether and/or propylene-glycol

solvents, for example, dipropylene glycol, tripropylene glycol, and mixtures thereof, and in combination with surfactants including ionic, non-ionic, amphoteric surfactants, or combinations thereof, such that the cleaning solvent or a mixture of solvents still remains water soluble and this can be completely rinsed off during the water rinse cycle.

Among these candidates, the methyl-ether solvents, DPM and TPM are essentially completely water soluble while the isopropyl ether solvents are sparingly soluble and the DPnB and TPnB are essentially insoluble in water. It is found that a single solvent, for example, DPM or TPM or mixture thereof, without any surface tension lowering additives are effective in cleaning paste residue on screening masks and paste processing equipment used in ceramic substrate production and in electronic circuit assembly. For removing highly hydrophobic paste residue from metal and plastic surfaces, tripropylene glycol butyl ether (TPnB) or dipropylene glycol butyl ether (DPnB) can be blended with TPM up to 20% by volume, and optionally adding a surfactant, was found effective when processed according to the semi-aqueous cleaning method according to this invention.

Tri-propylene-glycol methyl-ether (TPM) is a preferred organic solvent for the semi-aqueous cleaning method disclosed herein for polymer/metal composite paste residue removal but other related commonly known propylene glycol alkyl ethers that may also be used: di-propylene-glycol methyl-ether (DPM), tri-propylene-glycol butyl-ether (TPnB) or other propylene-glycol alkyl-ether solvents in combination with TPM so long as the mixed solvent system remains readily rinsable with water.

According to the preferred embodiments of this invention, the propylene-glycol alkyl-ether solvent used in the semi-aqueous has the following essential characteristics:

- Surface tension is less than about 40 dynes/cm
- Non-corrosive, no contact hazard concerns
- High boiling with flash point, above about 140° F.
- Low VOC (Volatile Organic Compound) potential
- Non-ODS (Ozone Depleting substance)
- Partially or completely soluble in water
- No detrimental effect on metal and plastic parts
- Compatible with solvent recovery and recycling
- Option for reclamation of paste metal solids
- Suitable for production or laboratory operations
- Can be used in conjunction with surfactants/additives.
- Tripropyleneglycol (TPM), a preferred solvent, has the following relevant physical properties:

Boiling point of about 243° C.; Flash point of about 121° C. (250° F.); and vapor pressure of about 25° C. at about 0.01 mm Hg.

The overall process involves ultrasonic or pressure spray cleaning of paste residue carrying substrates with a propylene glycol alkyl ether solvent which is followed by the first water rinse to replace the solvent on the surface of substrate with water, an optional second water rinse to remove any residual solvent, and then the final water rinse and hot air dry operations to provide clean and dry substrates for use in subsequent screening cycle. Cleaning Solvent bath life, i.e., number of cleaning cycles in the same liquid bath before solvent replacement depends on the frequency of use, type and number of parts being cleaned in one cycle and the total amount of paste residue removed per cycle.

The waste solvent from the cleaning process described herein contains soluble and insoluble paste constituents primarily metal and inorganic solids and dissolved paste organics. It has been found that the metal and inorganic

solids in the wash separate out in a readily filtrable form which can be removed by filtration or by first centrifuging followed by filtration. The filtered solvent contains dissolved organic constituents of the paste residue removed along with dissolved metals. As shown in FIG. 2, the solids-free solvent can be micro-filtered or passed through absorbing media, for example, activated charcoal, and reused at least once again to clean paste residue from screening masks and paste processing equipment. Alternatively, the waste solvent after solids removal can be subjected to distillation to recover essentially pure solvent which can be reused for cleaning, thus providing waste minimization, and material cost reduction.

The rinse water from the first rinse operation contains varying level of the cleaning solvent due to its carry-over from the cleaning bath, the relative wt % of which e.g., TPM, can be obtained by monitoring the surface tension which decreases as the amount of the solvent carry-over increases, for example, as TPM increases as shown in the calibration data in Tables 1 and 2, with graphical representation in FIGS. 4 and 5, respectively. It is found that the first water rinse bath can be continued to be used till the surface tension comes down to about 50 dynes/cm which corresponds to about 7 wt % TPM (calculated from the surface-tension/TPM concentration correlation shown in FIG. 4.) dissolved in water at which time, the used rinse water is replaced by fresh water. The semi-aqueous cleaning method for paste residue removal disclosed herein offers a major benefit such that it presents no safety issues, no corrosion and contact hazard concerns, relatively easy recycling of solvent because no or minimum amount of other additives, and rinse water, and thus allows reduced consumption of organic solvent, waste minimization, economic benefit, and water conservation. With the recycling of cleaning solvent and rinse water after purification, the semi-aqueous cleaning method disclosed herein has the potential for a close-loop system where the cleaning solvent as well as the rinse water are recovered and recycled. This is in contrast to cleaning with chlorinated solvents in addition to the environmentally hazardous volatile emission issues, the solids are disposed-off as hazardous waste which goes for landfill or it is incinerated.

TABLE 1

Percent DPM in Water	Surface Tension (dynes/cm)
0	77.6
0.5	64.5
1	61.8
3	56.4
4	54.8
5	53.4
6	52.3
7	50.9
10	48.9
Pure TPM	32.5

TABLE 2

Percent DPM in Water	Surface Tension (dynes/cm)
0	75.9
0.1	73.5
0.3	70.8
0.5	68.7
1	66.5

TABLE 2-continued

Percent DPM in Water	Surface Tension (dynes/cm)
3	58.8
5	57.4
7	53.8
10	50.9
Pure DPM	32.1

The mask cleaning method using TPM and related solvents also has several advantages over the multi-component aqueous alkaline solutions of prior art comprising alkali metal silicates, phosphates, and surfactants. Specifically, such ingredients in the commonly known aqueous detergent compositions have environmental issues, require costly, waste generating sludge forming wastewater treatment, and are not compatible with recovery from the effluent. These methods require the use of coagulants and flocculants, typically lime precipitation as Alum and iron salts, or PACLS (polyaluminum chloride), organic poly-electrolytes etc, to precipitate silicates, phosphates, and other suspended matter from wastewater which adds to solids loading of the waste. The 'sludge' or precipitated solids has associated disposal issues of landfill limitation, disposal cost, and if there is any heavy metal contamination, it becomes hazardous waste requiring higher cost of waste disposal.

Representative applications of the disclosed method are in the area of ceramic manufacturing, conductive paste screening, solder paste stencil printing for SMT, ultra fine pitch BGA, assembly solder paste applicators, and thermal paste cleaning.

The propylene-glycol alkyl-ether solvent of this invention would be a direct replacement of chlorinated hydrocarbon solvents, such as, perchloroethylene, aromatic hydrocarbon solvents, such as, xylene, and alcohol and ketone solvents, such as, methanol, ethanol, isopropanol, methyl ethyl ketone.

As stated earlier this invention allows the cleaning of screening masks and associated equipment by a semi-aqueous cleaning method employing a high boiling, low vapor pressure, substantially water soluble organic solvent to remove conductive paste residue in ceramic substrate manufacturing technology.

Similarly, this invention teaches the cleaning of paste residues in electronic circuit assembly, for example, solder paste stencil printing, solder paste application/dispensing for SMT, and ultra fine pitch BGA assembly, with a semi-aqueous cleaning method employing a high boiling, low vapor pressure, substantially water soluble organic solvent to remove conductive paste residue from solder paste applicators.

#### EXAMPLE

Various aspects of the present invention are further illustrated by referring to the following example which is intended only to further illustrate the invention and is not intended to limit the scope of the invention in any manner.

#### Example 1

Molybdenum metal masks having fine pitch etched features for via and wiring metallurgical patterns, and for I/O pads, suitable for multi-layer ceramic substrates were used for screening conductive pastes onto ceramic green sheet with a paste screening tool. Various conductive pastes used for screening in ceramic technology generally comprise of

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metal filler as the predominant component in a polymer binder-solvent system. Representative pastes screened onto green sheets using the metal masks contained between about 70 to about 85 percent metal powder filler, typically Molybdenum, Copper, Tungsten, and Nickel, in ethyl cel-  
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 ulose type polymer binders and a high boiling polar solvents, for example, 2,2,4-trimethylpentane diol 1,3-monoisobutyrate, or diethylene glycol alkyl ether acetate in conjunction with fatty acid ester based surfactant, thickening agents, and other additives like antioxidants, coloring  
 10  
 agents, corrosion inhibitors, etc. Also tested were non-polar conductive pastes based on low molecular weight thermo-  
 plastic resins derived from petroleum hydrocarbons as the binder in place of cellulosic binders in combination with hydrocarbon oil as solvent vehicle. Some of the pastes  
 15  
 tested, in addition to carrying metal powder as the major component also contained inorganic fillers such as glass, ceramic,  $\text{Al}_2\text{O}_3$ — $\text{SiO}_2$  glass-frit. After the paste screening operation, the masks carrying the paste residue on the surface and inside the etched features were cleaned with tripropyleneglycol monomethylether (TPM) as described in the following examples:

#### Example (A)

The solvent 12, was preheated to between about 55 to about 65° C. in the first ultrasonic tank 10, of the apparatus assembly 100, shown in FIG. 1, and the mask 25, mounted on a special handler 50, was submerged in the solvent 12, with XYZ robotic arm 75. Ultrasonics were then turned on for between about 2 and about 3 min or until the paste residue was removed from all areas of the mask 25. After the solvent cleaning, the mask 25, was transported to tank 20 (FIG. 1) for first water rinse 22, preferably de-ionized water 22, with ultrasonic on or other means of mechanical agitation to accelerate the carry-over solvent displacement with water. Optionally, the mask 25, is then transported to the second rinse tank (tank 30), followed by final water rinse 42, in tank 40, and dry by forced hot air or  $\text{N}_2$ , at station 60. Microscopic inspection of the cleaned masks 25, showed no evidence of paste residue in any area of the masks 25.

#### Example (B)

Similar process as discussed in Example 1, was used for cleaning screening paste residue from paste applicators and other processing parts/equipment 25, which required up to between about 5 to about 10 min ultrasonic agitation for complete removal of the paste from all areas. The cleaning process could be accelerated by using ultrasonic with immersion pressure spray with single or multi-nozzle systems, followed by water rinse and drying cycles and described in Example 1(A). Microscopic inspection of cleaned and dried parts 25, showed no evidence of paste residue in any area of the parts 25.

While the present invention has been particularly described, in conjunction with a specific preferred embodiment, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art in light of the foregoing description. It is therefore contemplated that the appended claims will embrace any such alternatives, modifications and variations as falling within the true scope and spirit of the present invention.

What is claimed is:

1. A method for cleaning a conductive or soldering paste from at least one object used in the fabrication of semiconductor packaging substrates, organic chip carriers or cards, the method comprising the steps of:

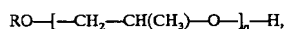
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immersing said object in a solvent consisting of at least one dipropylene glycol alkyl ether and at least one tripropylene glycol alkyl ether; and

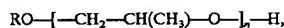
rinsing said object in water, thereby cleaning said paste from said object;

wherein said object is selected from a group consisting of screening mask, paste processing parts used in the production of ceramic substrates or plastic substrates, screen stencils, stencil printing equipment, paste dispense equipment, paste making equipment, paste processing equipment, metal substrate, ceramic substrate and plastic substrate.

2. The method of claim 1, wherein said at least one dipropylene glycol alkyl ether has a general formula:



where R is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$  or  $\text{C}_4\text{H}_9$ , and n is 2, and said at least one tripropylene glycol alkyl ether has a general formula:



where R is  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$  or  $\text{C}_4\text{H}_9$ , and n is 3.

3. The method of claim 1, wherein said at least one dipropylene glycol alkyl ether and said at least one tripropylene glycol alkyl ether are partially or completely soluble in water.

4. The method of claim 1, wherein said at least one dipropylene glycol alkyl ether and said at least one tripropylene glycol alkyl ether are selected from a group consisting of di-propylene-glycol methylether, tri-propylene-glycol methyl-ether, and mixtures thereof.

5. The method of claim 1, wherein said tripropylene glycol alkyl ether is tri-propylene-glycol methyl-ether in admixture with tri-propylene-glycol butyl-ether.

6. The method of claim 1, wherein said paste is selected from a group consisting of a polymer/filler composite of metal, a solvent vehicle and a surfactant/dispersant, thickening agent, antioxidant, and corrosion inhibitor.

7. The method of claim 1, wherein said paste is a conductive screening paste comprising a metal filler selected from a group consisting of Ag, Au, Mo, W, Cu and Cu/Ni; a cellulosic polymer binder; a solvent carrier; and a dispersing agent.

8. The method of claim 1, wherein said paste is a conductive screening paste having at least one metal filler selected from a group consisting of Pb—Sn, Bi—Sn, Pb—In, Ag, Au, Mo, W, Cu and Cu/Ni.

9. The method of claim 1, wherein said paste comprises at least one organic binder.

10. The method of claim 1, wherein said paste is a polymer/metal composite paste.

11. The method of claim 1, wherein said at least one dipropylene glycol alkyl ether and said at least one tripropylene glycol alkyl ether is selected from the group consisting of dipropyleneglycol methylether (DPM), tripropyleneglycol methylether (TPM), dipropyleneglycol ethylene, tripropyleneglycol eneglyether, tripropyleneglycol isopropylether, dipropyleneglycol isopropylether, dipropyleneglycol n-butylether (DpnB), and tripropyleneglycol n-butylether (TpnB).

12. The method of claim 8, wherein said conductive screening paste is at least one solder paste comprising Pb—Sn, Bi—Sn or Pb—In alloy as the metal filler, at least one fluxing agent and a solvent, and optionally a polymer binder.

13. A method for cleaning a conductive or soldering paste from at least one object used in the fabrication of semicon-



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ductor packaging substrates, organic chip carriers or cards, the method comprising the steps of:

- (a) pre-heating a solvent consisting of at least one dipropylene glycol alkyl ether and at least one tripropylene glycol alkyl ether in a first tank having at least one ultrasonic bath, wherein said solvent is pre-heated to a temperature of about 45 to about 80° C.,
  - (b) immersing said object in said pre-heated solvent and subjecting said object to ultrasonic agitation for a time of about 1 to about 10 min, and
  - (c) transferring said object to a second tank having water pre-heated to a temperature of about 45 to about 70° C., and subjecting said object to at least one of immersion spray and ultrasonic agitation, thereby cleaning said paste from said object;
- wherein said object is selected from a group consisting of screening mask, paste processing parts used in the production of ceramic substrates or plastic substrates, screen stencils, stencil printing equipment, paste dispense equipment, paste making equipment, paste processing equipment, metal substrate, ceramic substrate and plastic substrate.

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14. The method of claim 13, wherein in step (c) said object is subjected to said at least one of immersion spray and ultrasonic agitation, for a time of about 30 sec to about 120 sec.

15. The method of claim 13, further comprising, after step (c), the step of transferring said object from said second tank to at least one third tank having water and subjecting said object to at least one of spray rinsing and ultrasonic agitation.

16. The method of claim 13, further comprising the step of filtering said solvent to remove particulate material.

17. The method of claim 13, wherein said second tank having water can be used until surface tension exceeds about 50 dynes/cm.

18. The method of claim 13, further comprising the step of discharging said water from said second tank.

19. The method of claim 15, wherein said object is subjected to at least one of spray rinsing and ultrasonic agitation, for a time of about 30 sec to about 120 sec.

20. The method of claim 16, further comprising the step of distilling said solvent to recover said solvent for reuse.

\* \* \* \* \*



# United States Patent [19]

Austin et al.

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[45] Date of Patent: Jul. 17, 1990

[54] METHOD OF ANISOTROPICALLY  
ETCHING SILICON WAFERS AND WAFER  
ETCHING SOLUTION

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C09K 13/00; C03C 15/00

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156/657; 156/659.1; 156/662; 252/79.1;  
252/79.4

[58] Field of Search ..... 156/647, 657, 659.1,  
156/662, 628; 252/79.1, 79.2, 79.4, 79.5;  
437/225, 228, 233

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Primary Examiner—William A. Powell

Attorney, Agent, or Firm—William D. Sabo

[57] ABSTRACT

An improved method for anisotropically etching the  
(100) crystallographic plane of silicon wafers, involves  
immersing the wafers in an etching solution containing  
an aromatic compound having at least two adjacent  
hydroxyl groups and a polar functional group on the  
ring, an amine and water. A quality etch at an apprecia-  
bly greater rate is achieved.

28 Claims, No Drawings

# METHOD OF ANISOTROPICALLY ETCHING SILICON WAFERS AND WAFER ETCHING SOLUTION

## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

This invention relates to the etching of silicon, and, more particularly, to the improved anisotropic etching of single crystal silicon.

### 2. Description of the Prior Art

The anisotropic etching of single crystal silicon has been carried out for many years in the production of microelectronic devices. An essential feature is that the etching solution etch the (100) crystallographic plane at an appreciably greater rate than the (110) and (111) planes, producing v-shaped sidewalls at 54.74° from the (100) surface. Exemplificative of the solutions which are known in the art are the following: IBM Tech. Disc. Bull., Vol. 19, No. 9 (February 1977), p. 3623 discloses a solution for anisotropically etching single crystal silicon, containing ethylene diamine, pyrocatechol and water; and IBM Tech. Disc. Bull., Vol. 19, No. 10 (March 1977), p. 3953 also describes such a solution, containing the three ingredients described in the preceding article, but further including hydrogen peroxide.

See also, U.S. Pat. Nos. 4,417,946, issued to Bohlen et al on Nov. 29, 1983, and 4,342,817, issued to Bohlen et al on Aug. 3, 1982, both of which disclose a method of making a mask, employing an etching solution consisting of ethylene diamine, pyrocatechol, water, and, optionally, hydrogen peroxide; and U.S. Pat. Nos. 4,293,373, issued to Greenwood on Oct. 6, 1981, and 4,229,979, issued to Greenwood on Oct. 28, 1980, both of which disclose a method of making a silicon transducer which involves etching a boron doped silicon wafer, with a solution containing ethylene diamine, pyrocatechol and water.

Note also, U.S. Pat. No. 3,650,957, issued to Shipley, Jr. et al on Mar. 21, 1972, which discloses a solution for etching copper, which includes a source of cupric ions, a complexing agent for cupric ions, such as a hydroxycarboxylic acid or an alkanolamine, a source of chloride or bromide ions and a solution soluble molybdenum, tungsten or vanadium compound.

U.S. Pat. No. 3,873,203, issued to Stevenson on Mar. 25, 1975, discloses a mixture for etching silicon, containing hydrazine and pyrocatechol.

Further, U.S. Pat. No. 3,160,539, issued to Hall et al on Dec. 8, 1964, relates to an etching solution for silicon, which includes piperidine.

IBM Tech. Disc. Bull., Vol. 15, No. 1 (June 1972), p. 173 discloses an etchant for aluminum, consisting of a solution of a secondary organic amine, such as piperidine or pyrrolidine, in water.

In addition, a particularly effective solution for etching single crystal silicon is disclosed in U.S. patent application Ser. No. 875,833, filed by Beechko on June 18, 1986. That solution comprises ethanolamine, pyrocatechol, water, hydrogen peroxide and piperidine. It has been found that the solution etches (100) silicon at a rate of about 40  $\mu$ /hr.

## BRIEF SUMMARY OF THE INVENTION

Now, an improved method of etching silicon has been developed which involves contacting the silicon with an etching solution which comprises an aromatic

compound having at least two adjacent hydroxyl groups and a polar functional group on the ring, an amine and water. The present invention is also directed to the etching solution per se.

In accordance with the invention, an etch rate for (100) silicon of about 125–140  $\mu$ /hr. has been achieved. This rate is, for example, more than three times greater than that normally obtained by employing the etching solution of the above-noted Beechko application. Moreover, the etching solution is relatively safe in manufacturing use and environmentally compatible with current disposal techniques.

## DETAILED DESCRIPTION

In the practice of the invention, silicon wafers to be etched are preferably immersed in the etching solution. Preferably, this is carried out at a temperature of about 100°–125° C., more preferably of about 115°–125° C. The actual temperature and time may vary, however, depending upon a number of factors, such as the desired etch rate, the geometry being etched, the exact formulation employed, and so forth, as will be apparent to those skilled in the art. In addition, the pH of the solution preferably ranges from about 11–12 in most situations.

As noted above, the etching solution employed according to the present invention includes an aromatic compound having at least two adjacent hydroxyl groups and a polar functional group on the ring. Typically, the polar functional group is COOH, SO<sub>2</sub>OH or NO<sub>2</sub>, with COOH being preferred. Suitable aromatic compounds include, for example, the following:

1,2-dihydroxybenzene-3,5-disulfonic acid;  
6,7-dihydroxy-2-naphthalenesulfonic acid;  
3,4-dihydroxybenzoic acid;  
2,3-dihydroxybenzoic acid;  
2,3,4-trihydroxybenzoic acid;  
4-nitrocatechol; and  
esculetin (6,7-dihydroxycoumarin).

In a particularly preferred embodiment, the aromatic compound is gallic acid.

Any suitable amine compound with a relatively high polarity may be employed in the etching solution of the invention. Suitable amines include, for example, the following:

a. The primary aliphatic amines including mono-, di-, and triamines. These amines usually contain 2–8, and preferably 2–6, carbon atoms such as ethylamine, n-propylamine, n-butylamine, n-amylamine, n-hexylamine, ethylene diamine, diaminopropane, diaminobutane, pentamethylene diamine, m-xylylenediamine and diethylene triamine. Particularly preferred amines in this group are the diamines having 2–4 carbon atoms such as ethylene diamine and diaminopropane.

b. The alkanolamines, i.e., the aliphatic hydroxy amines. Usually each alkanol group in these amines contains from 2 to 5 carbon atoms. Illustrative are monoethanolamine, diethanolamine, triethanolamine, the mono-, di-, and tripropanolamines, ethanolpropanolamine, diethanolpropanolamine, and the mono-, di-, and tributanolamines. Particularly preferred alkanolamines are those in which each alkanol group contains 2–3 carbon atoms such as the ethanolamines, the propanolamines and the ethanolpropanolamines.

In a particularly preferred embodiment of the invention, monoethanolamine is employed.

Although the proportions of the ingredients may vary over wide ranges, the etching solution preferably

contains about 3-6 mole percent of the aromatic compound, about 32-56 mole percent of the amine and about 65-38 mole percent of water. More preferably, the etching solution contains about 4-6 mole percent of the aromatic compound, about 39-56 mole percent of the amine and about 57-38 mole percent of water.

Various other ingredients may be added to the etching solution. For example, a small amount, such as about 0.2-0.3 mole percent, of pyrazine or piperidine or of hydrogen peroxide (e.g., 0.5-3 ml/1000 ml of amine compound) may be added in order to further enhance the etch rate of the solution. In addition, a small amount of a surfactant (e.g., 0.5-3 ml/1000 ml of amine compound), such as "FC-129", commercially available from Minnesota Mining & Manufacturing Company, or other fluorinated hydrocarbon surfactants, may be added. The presence of surfactant is desirable because it provides an increase in uniformity of etching, apparently by inhibiting adhesion of evolving hydrogen bubbles at the etching surface.

The etching solution of the invention provides a quality etch, i.e. with minimal pits, hillocks and faceting, and at a significantly faster rate. As such, it is desirable for use in a number of applications. For example, the etching solution can also be used to etch P-doped silicon wafers in the manner described in U.S. Pat. No. 4,342,817, the entire disclosure of which is incorporated herein by reference.

In one preferred application, the etching solution can be used to etch (100) silicon at a high rate (about 125-140  $\mu$ /hr.), while stopping at highly doped boron interfaces, allowing production of large, thin boron-rich windows on the surface of thick silicon wafers. These silicon products are useful in the manufacture of x-ray and e-beam masks.

Besides etching single crystal silicon, the etching solution of the invention is also effective in etching other silicon, such as polycrystalline silicon or epitaxial silicon.

The following examples are provided to illustrate the invention.

#### EXAMPLE 1

A pyrex reaction vessel (250 mm $\times$ 200 mm) was charged with 3 liters of monoethanolamine and 600 ml of deionized water. 900 Grams of gallic acid was added through a powder funnel, and the funnel rinsed with an additional 300 ml of deionized water. 20 Grams of pyrazine, 4.5 ml of surfactant ("FC-129") and 7.5 ml of 30% hydrogen peroxide were added, and the amber solution was brought to reflux under a water condenser.

Silicon wafers having a (100) crystallographic orientation were etched by immersing the wafers in the etching solution at a temperature of about 118°-120° C. for about 4 to 4.5 hrs. The etching solution etched (100) silicon at a rate of about 94  $\mu$ /hr. See Table I below.

#### EXAMPLE 2

A pyrex reaction vessel (250 mm $\times$ 200 mm) was charged with 1400 ml of deionized water, 1150 grams of gallic acid, 25 grams of pyrazine, 3800 ml of monoethanolamine and 7 ml of surfactant ("FC-129") The solution was heated to reflux under a water condenser.

Silicon wafers having a (100) crystallographic orientation were etched by immersing the wafers in the etching solution at a temperature of about 119° C. for about 5.5 hrs. The etching solution etched (100) silicon at a rate of about 125  $\mu$ /hr. See Table I below.

#### EXAMPLE 3

A 500 ml pyrex reaction kettle was charged with 335 ml of monoethanolamine and 75 ml of deionized water. 100.4 Grams of gallic acid was added through a powder funnel. 25 Ml of piperidine, 1 ml of surfactant ("FC-129") and 3 ml of 30% hydrogen peroxide were added, and the amber solution was brought to reflux under a water condenser.

Silicon wafers having a (100) crystallographic orientation were etched by immersing the wafers in the etching solution at a temperature of about 125° C. for about 10 hrs. The etching solution etched (100) silicon at a rate of about 60-70  $\mu$ /hr. See Table I below.

#### COMPARATIVE EXAMPLES A-G

For purposes of comparison, the procedure of Example 3 was repeated using the formulations as shown in Table I. In each Comparative Example, an aromatic compound, other than as defined in the description above was used in the formulation in place of gallic acid. In each case, the etch rate results for (100) silicon were found to be unacceptable. The formulations and the corresponding results are summarized in Table I below.

TABLE I

	Example			Comparative Example						
	I	2	3	A	B	C	D	E	F	G
Formulation										
Monoethanolamine	X	X	X	X	X	X	X	X	X	X
Piperidine			X	X	X	X	X	X	X	X
Pyrazine	X	X		X	X	X	X	X	X	X
Water	X	X	X	X	X	X	X	X	X	X
Surfactant (FC-129)	X	X	X	X	X	X			X	X
Hydrogen Peroxide	X		X	X	X	X			X	X
Gallic Acid	X	X	X							
Quinhydrone					X					
1,2-Naphthoquinone-4-Sulfonic Acid						X				
Alizarin							X			
Quinalizarin								X		
2,3-Dihydroxypyridine									X	
3,6-Dihydroxy-pyridazine				X						
1,2-Naphthoquinone										X
Catechol					X					
Etch Results*										
Etch Rate ( $\mu$ /hr)	94	125	60-70	S	N	N	N	N	NS	VS

\*The following abbreviations have been used:

S: Slow

N: None

VS: Very Slow

NS: Non-Selective

#### EXAMPLES 4-8

The procedure of Example 1 was followed by using the same ingredients in the same relative proportions, except that the amount of water in the solution was varied. The results are summarized in Table II below.

TABLE II

Example	Amount of Water (Mole Percent)	Etch Rate ( $\mu$ /hr)
4	41	113
5	46	133
6	51	140
7	53	140
8	57	137

We claim:

1. A method of etching silicon, comprising contacting said silicon with an etching solution which comprises an aromatic compound having at least two adjacent hydroxyl groups and a polar functional group on the ring, an amine and water.

2. The method of claim 1, wherein said polar functional group is COOH.

3. The method of claim 2, wherein said aromatic compound is gallic acid.

4. The method of claim 1, wherein said amine is selected from the group consisting of a diamine having 2-4 carbon atoms and an alkanolamine in which each alkanol group contains 2-3 carbon atoms.

5. The method of claim 4, wherein said amine is monoethanolamine.

6. The method of claim 1, wherein said etching solution further comprises pyrazine or piperidine.

7. The method of claim 1, wherein hydrogen peroxide is added to said etching solution.

8. The method of claim 1, wherein a surfactant is added to said etching solution.

9. The method of claim 1, wherein said etching solution comprises about 4-6 mole percent of said aromatic compound, about 39-56 mole percent of said amine and about 57-38 mole percent of water.

10. The method of claim 1, wherein said etching solution has a temperature of about 115°-125° C. and has a pH of about 11-12.

11. A method of etching a silicon wafer, comprising introducing said wafer into an etching solution which comprises about 4-6 mole percent of an aromatic compound having at least two adjacent hydroxyl groups and a COOH group on the ring, about 39-56 mole percent of an amine selected from the group consisting of a diamine having 2-4 carbon atoms and an alkanolamine in which each alkanol group contains 2-3 carbon atoms and about 57-38 mole percent of water.

12. The method of claim 11, wherein said aromatic compound is gallic acid and said amine is monoethanolamine.

13. The method of claim 12, wherein said etching solution has a temperature of about 115°-125° C. and has a pH of about 11-12.

14. The method of claim 13, wherein said etching solution further comprises pyrazine or piperidine.

15. The method of claim 14, wherein hydrogen peroxide is added to said etching solution.

16. The method of claim 15, wherein a surfactant is added to said etching solution.

17. An etching solution for silicon, comprising an aromatic compound having at least two adjacent hydroxyl groups and a polar functional group on the ring, an amine and water.

18. The etching solution of claim 17, wherein said polar functional group is COOH.

19. The etching solution of claim 18, wherein said aromatic compound is gallic acid.

20. The etching solution of claim 17, wherein said amine is selected from the group consisting of a diamine having 2-4 carbon atoms and an alkanolamine in which each alkanol group contains 2-3 carbon atoms.

21. The etching solution of claim 20, wherein said amine is monoethanolamine.

22. The etching solution of claim 17, further comprising pyrazine or piperidine.

23. The etching solution of claim 17, further comprising a surfactant.

24. The etching solution of claim 17, comprising about 4-6 mole percent of said aromatic compound, about 39-56 mole percent of said amine and about 57-38 mole percent of water.

25. An etching solution for silicon, comprising about 4-6 mole percent of an aromatic compound having at least two adjacent hydroxyl groups and a COOH group on the ring, about 39-56 mole percent of an amine selected from the group consisting of a diamine having 2-4 carbon atoms and an alkanolamine in which each alkanol group contains 2-3 carbon atoms and about 57-38 mole percent of water.

26. The etching solution of claim 25, wherein said aromatic compound is gallic acid and said amine is monoethanolamine.

27. The etching solution of claim 26, further comprising pyrazine or piperidine.

28. The etching solution of claim 27, further comprising a surfactant.

\* \* \* \* \*



US005972123A

# United States Patent [19] Verhaverbeke

[11] Patent Number: **5,972,123**  
[45] Date of Patent: **Oct. 26, 1999**

## [54] METHODS FOR TREATING SEMICONDUCTOR WAFERS

[75] Inventor: Steven Verhaverbeke, Radnor, Pa.

[73] Assignee: CFMT, Inc., Wilmington, Del.

[21] Appl. No.: 09/096,898

[22] Filed: Jun. 12, 1998

### Related U.S. Application Data

[60] Provisional application No. 60/050,076, Jun. 13, 1997.

[51] Int. Cl.<sup>6</sup> B08B 3/12; B08B 3/08

[52] U.S. Cl. 134/3; 134/1; 134/99.1;  
438/750

[58] Field of Search 134/3, 1, 99.1;  
438/714, 749, 475

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Primary Examiner—Jill Warden

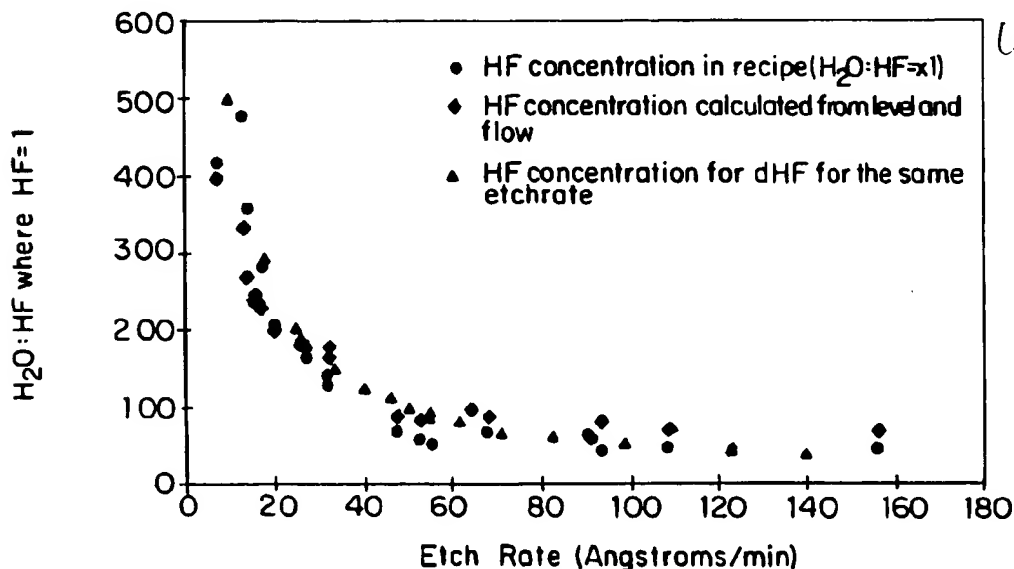
Assistant Examiner—Yolanda E. Wilkins

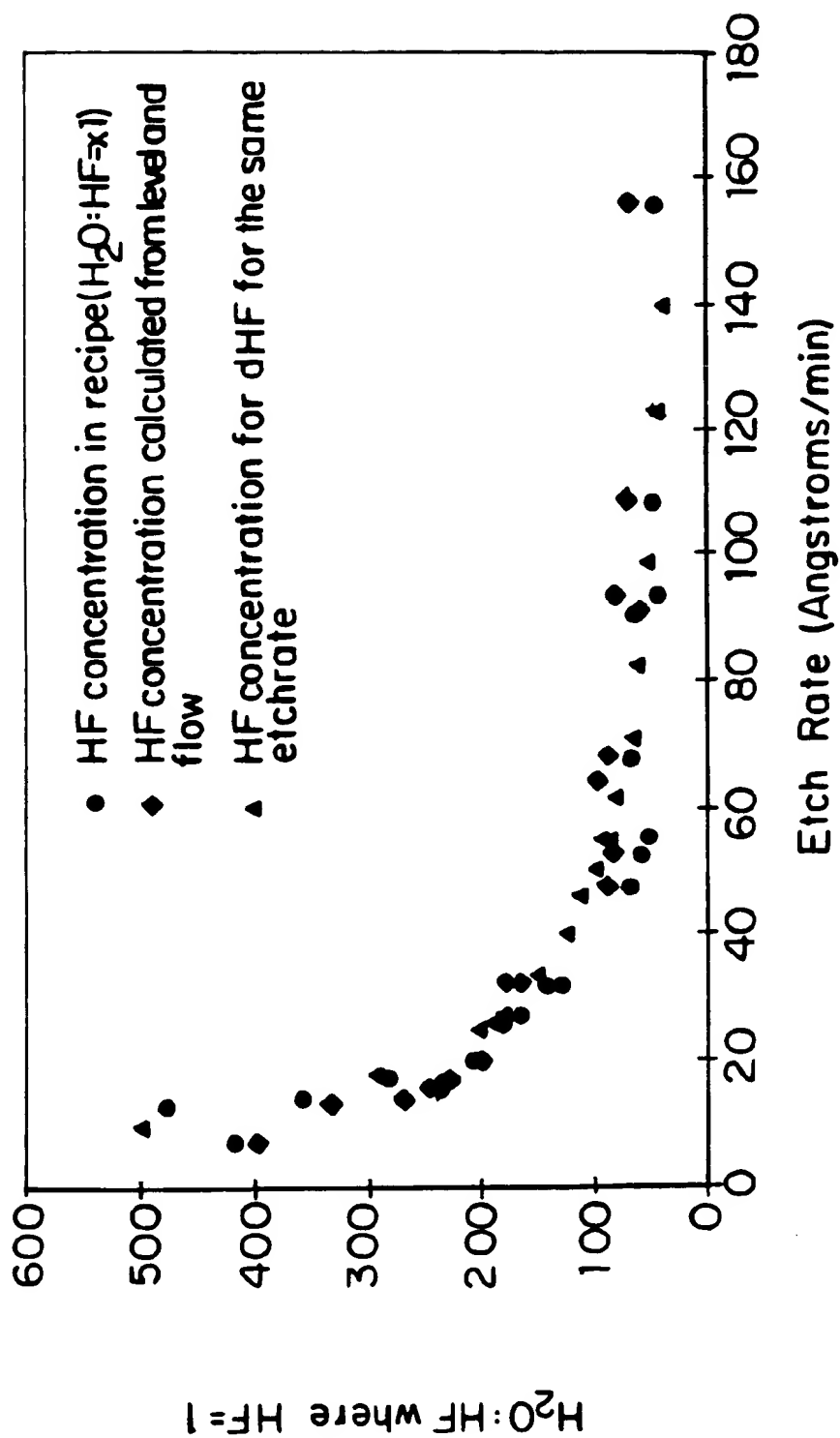
Attorney, Agent, or Firm—Woodcock Washburn Kurtz Mackiewicz & Norris LLP

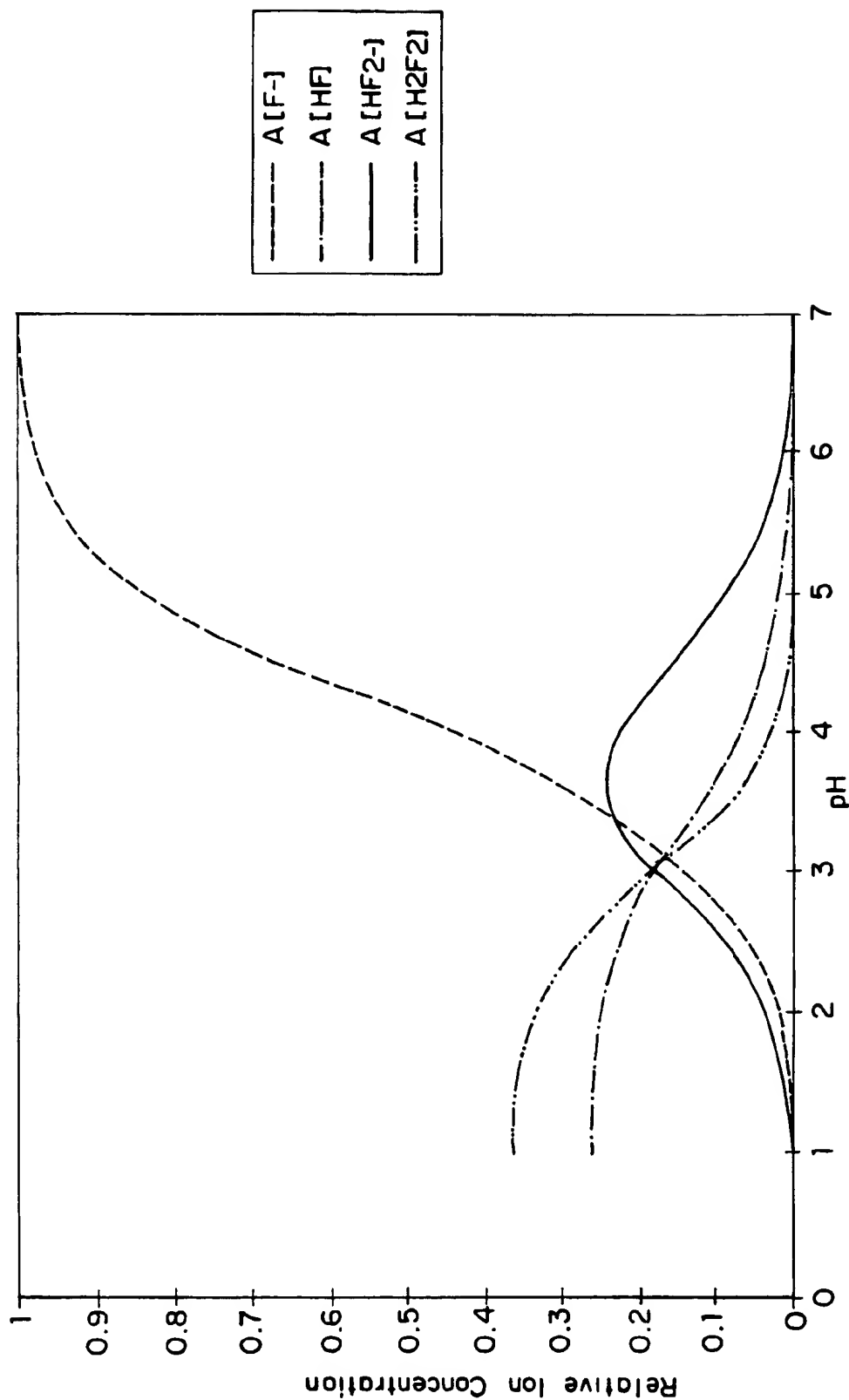
### [57] ABSTRACT

The present invention presents methods for, inter alia, cleaning and etching semiconductor wafers with a solution containing ammonium fluoride and control of the process used for preparing such a solution at its point of use.

10 Claims, 10 Drawing Sheets



**FIG. 1**

**FIG. 2**

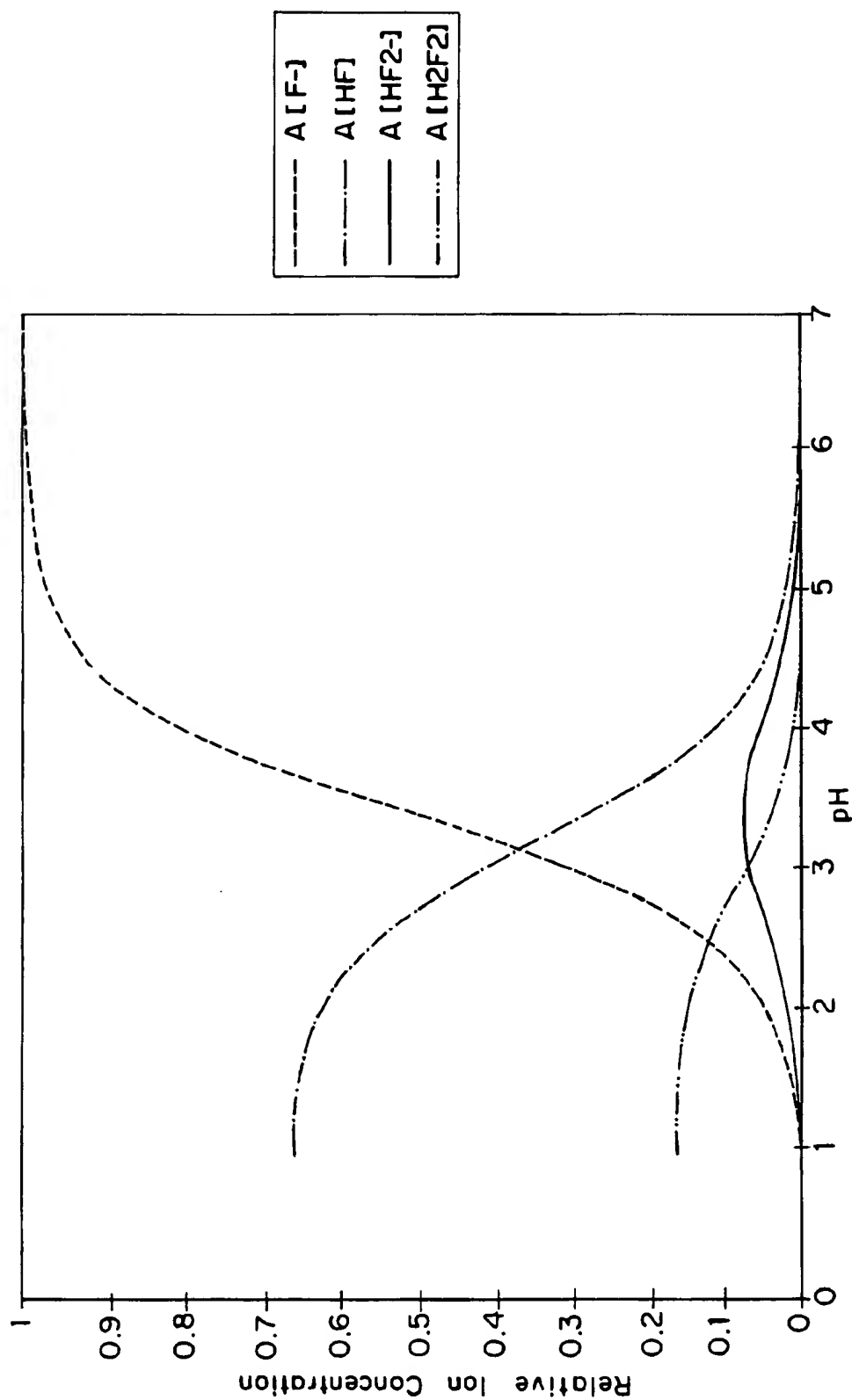
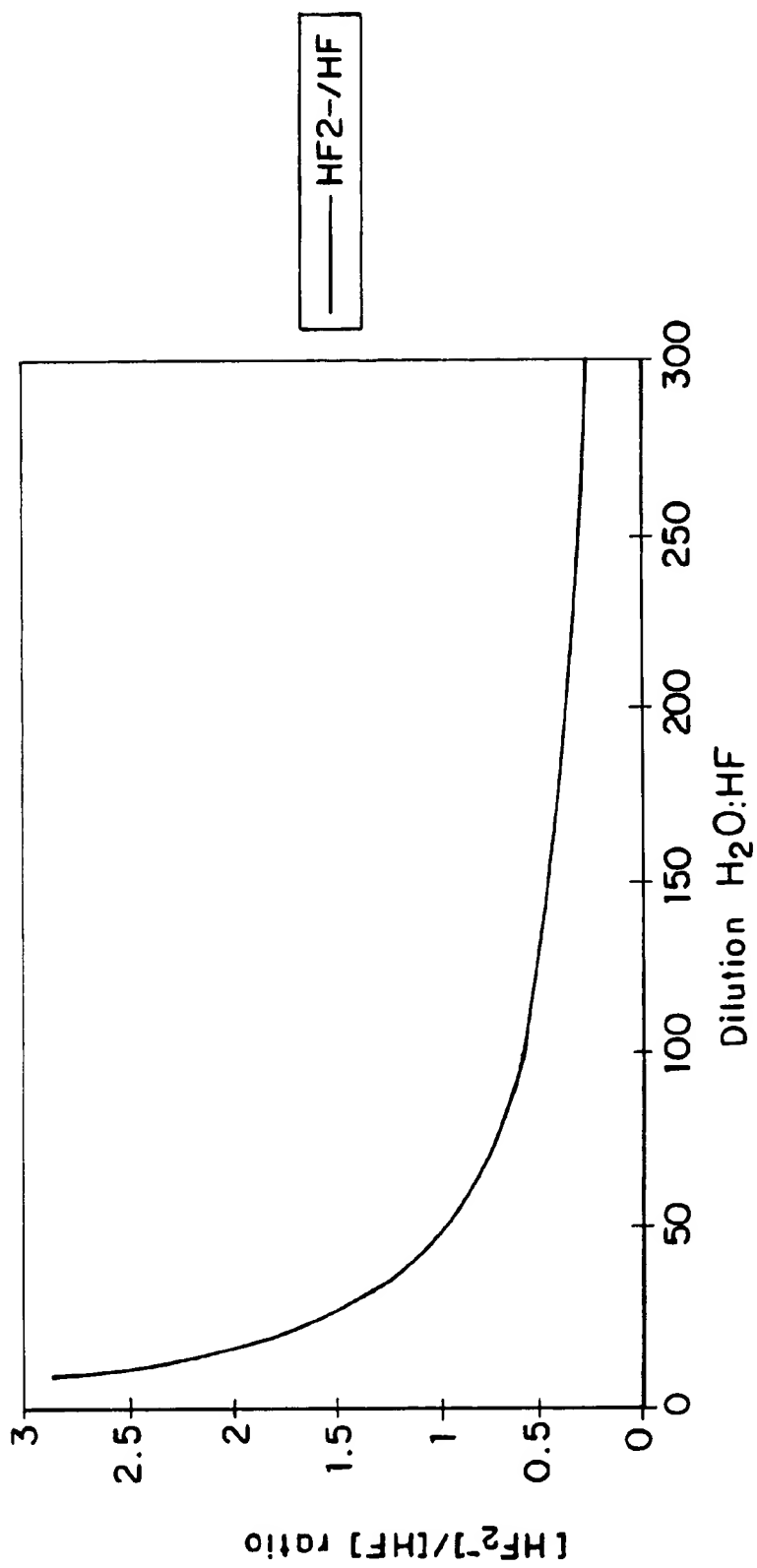


FIG. 3



**FIG. 4**

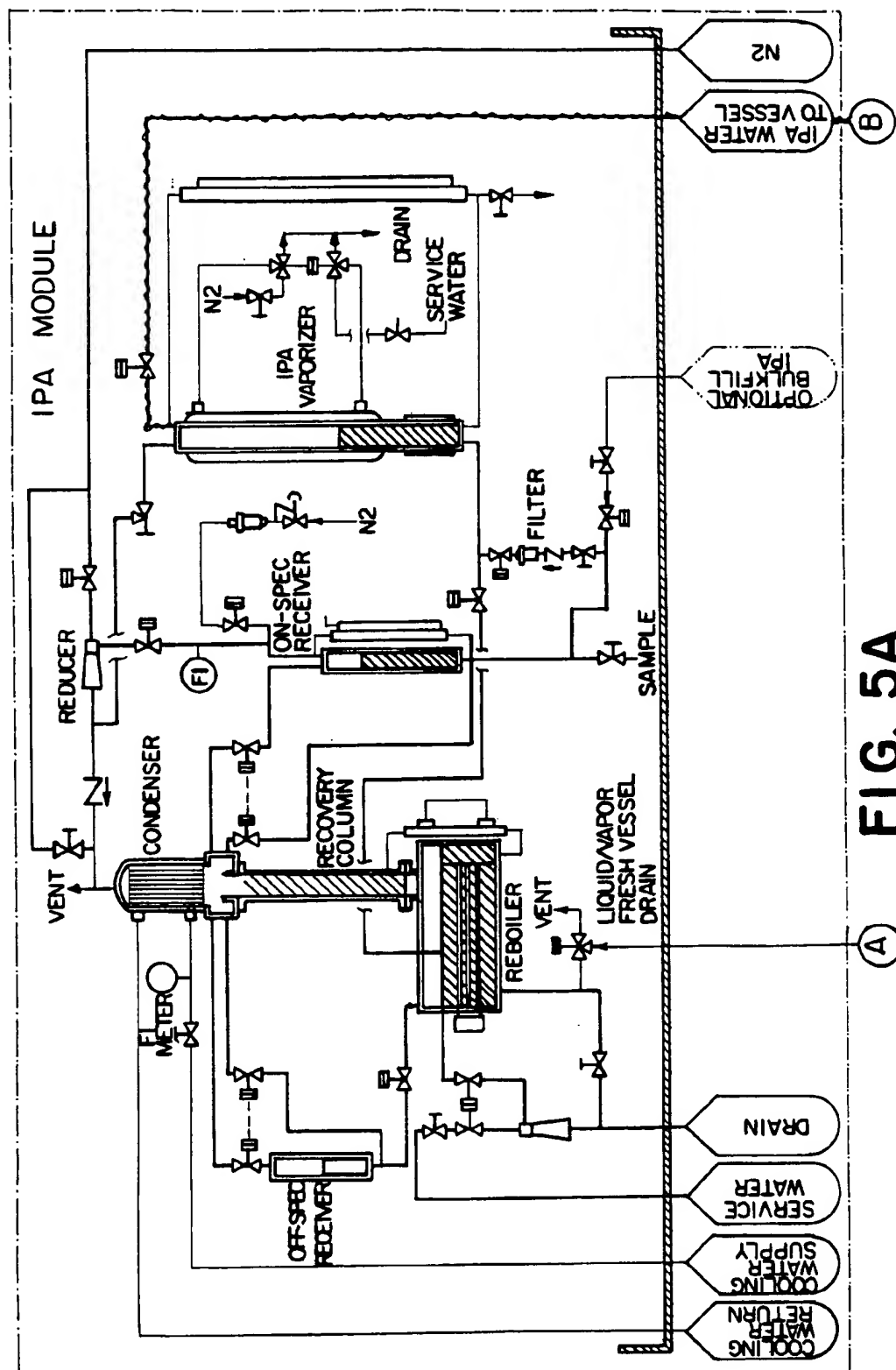
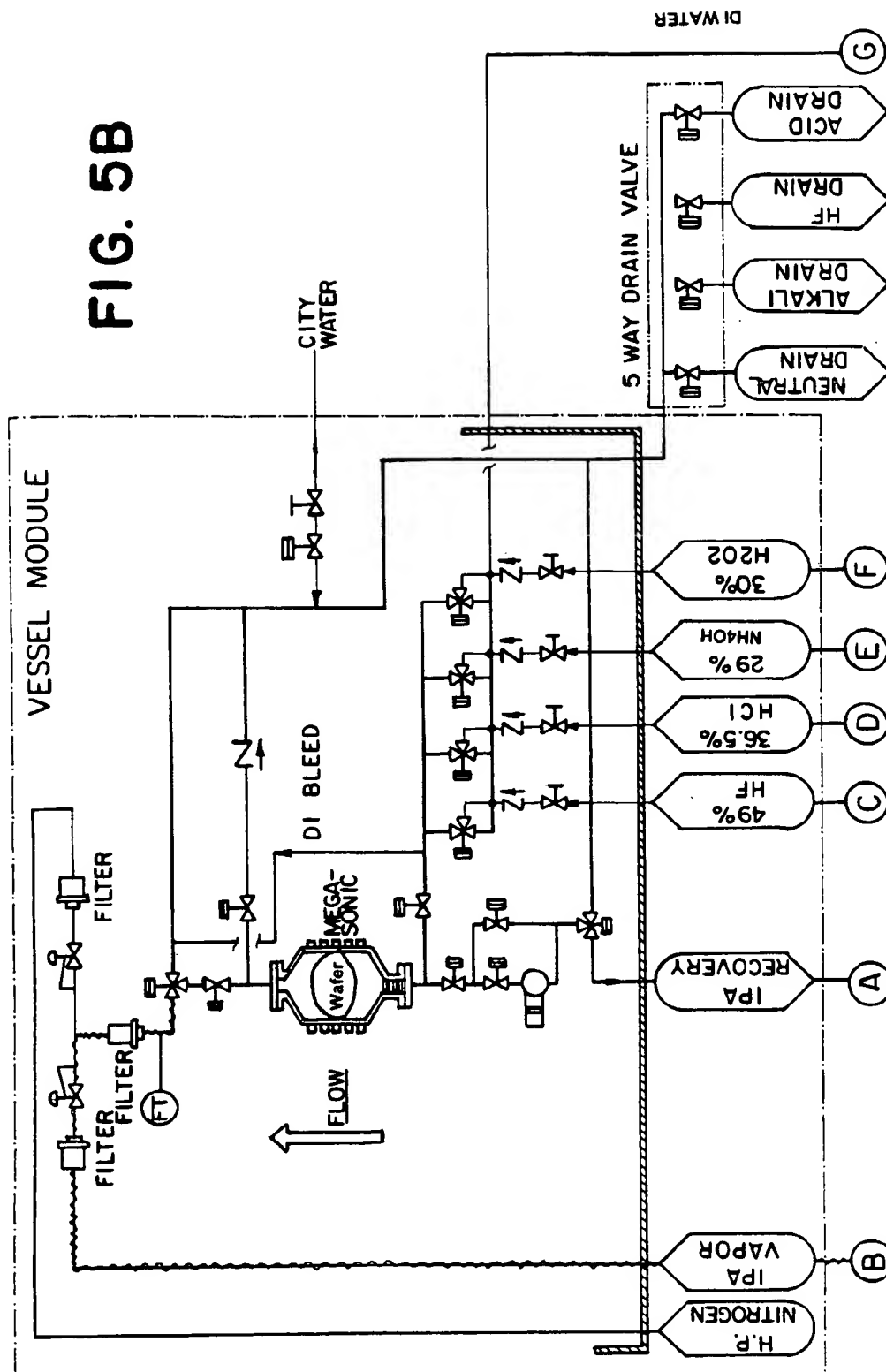


FIG. 5A



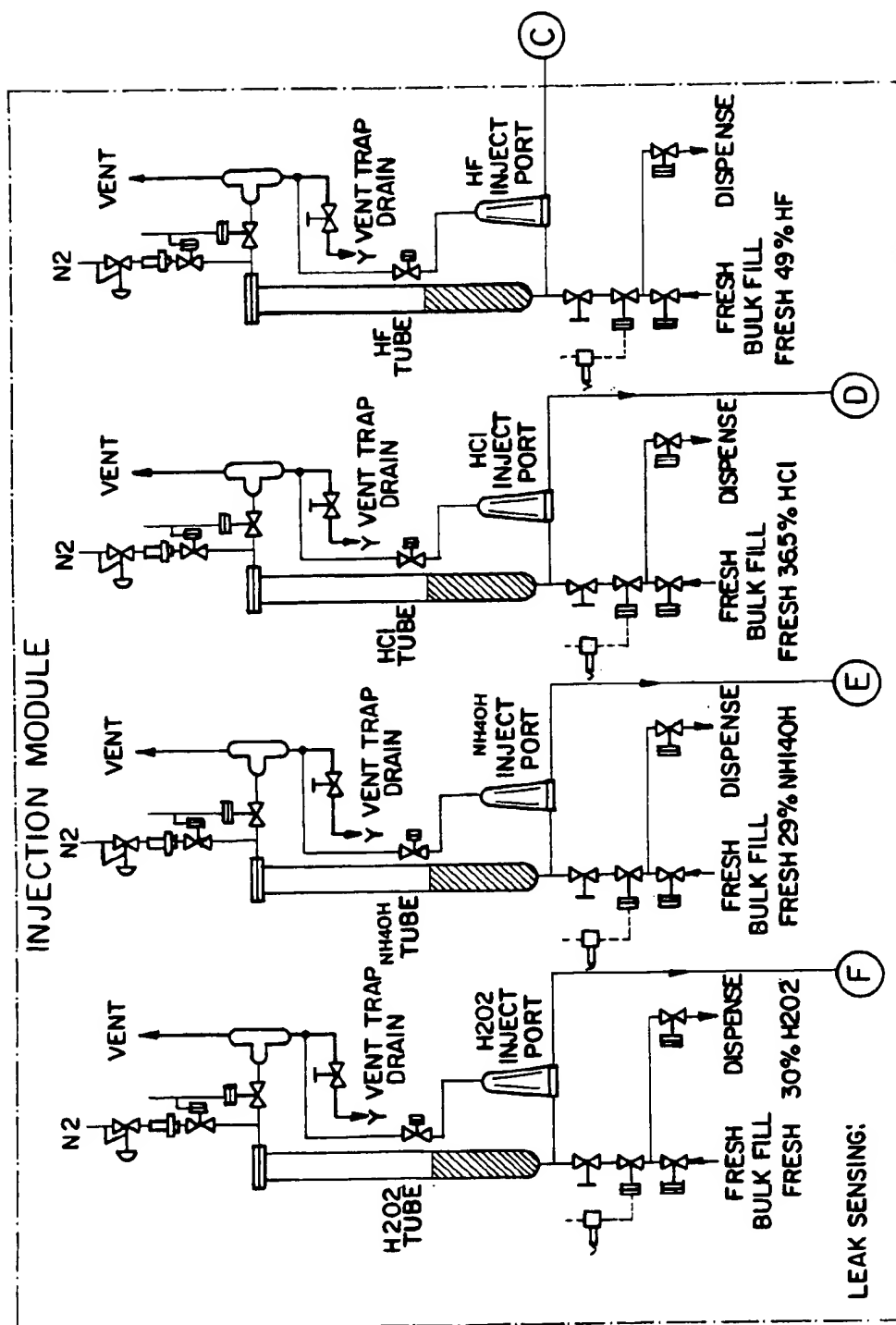
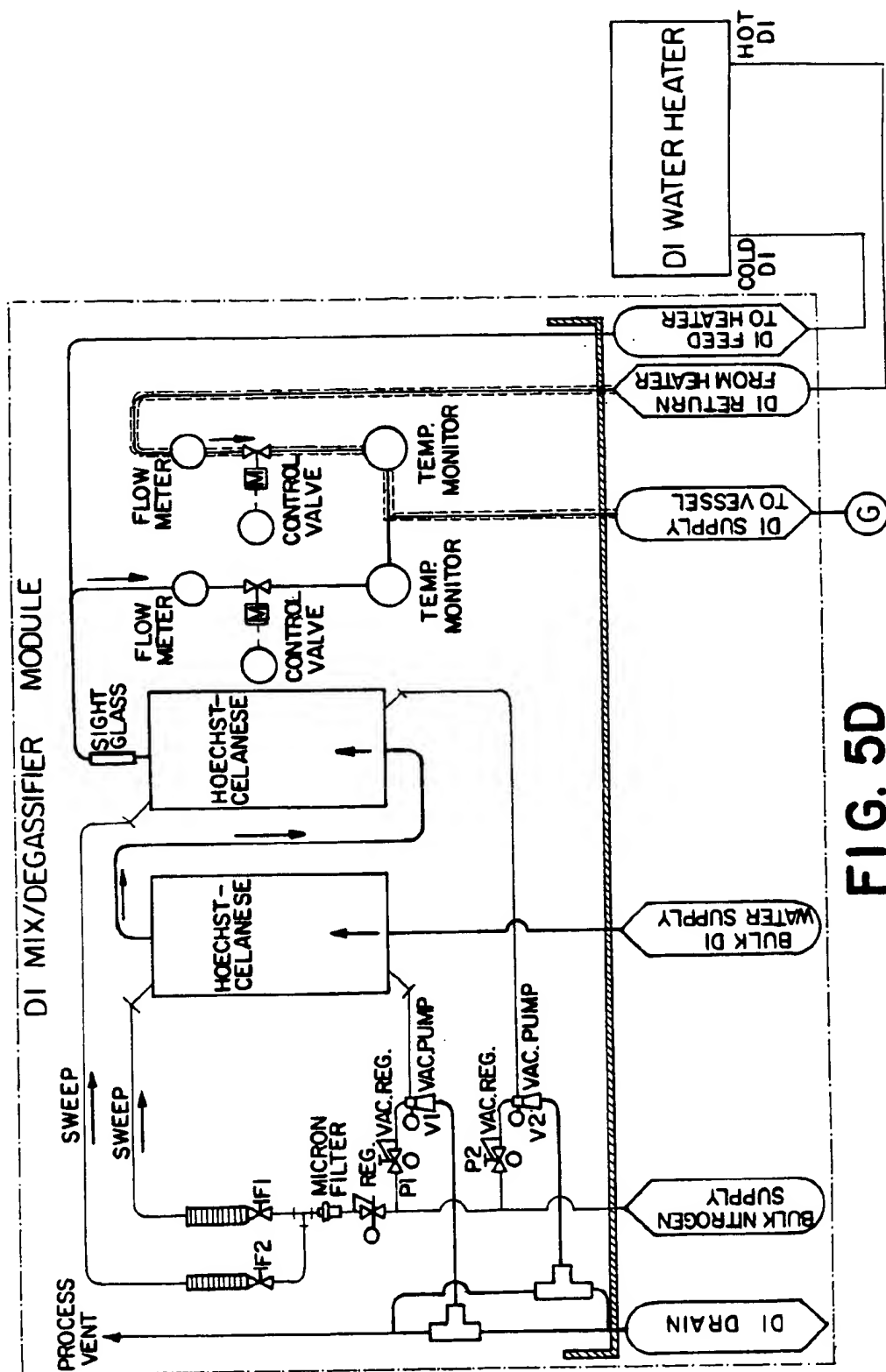
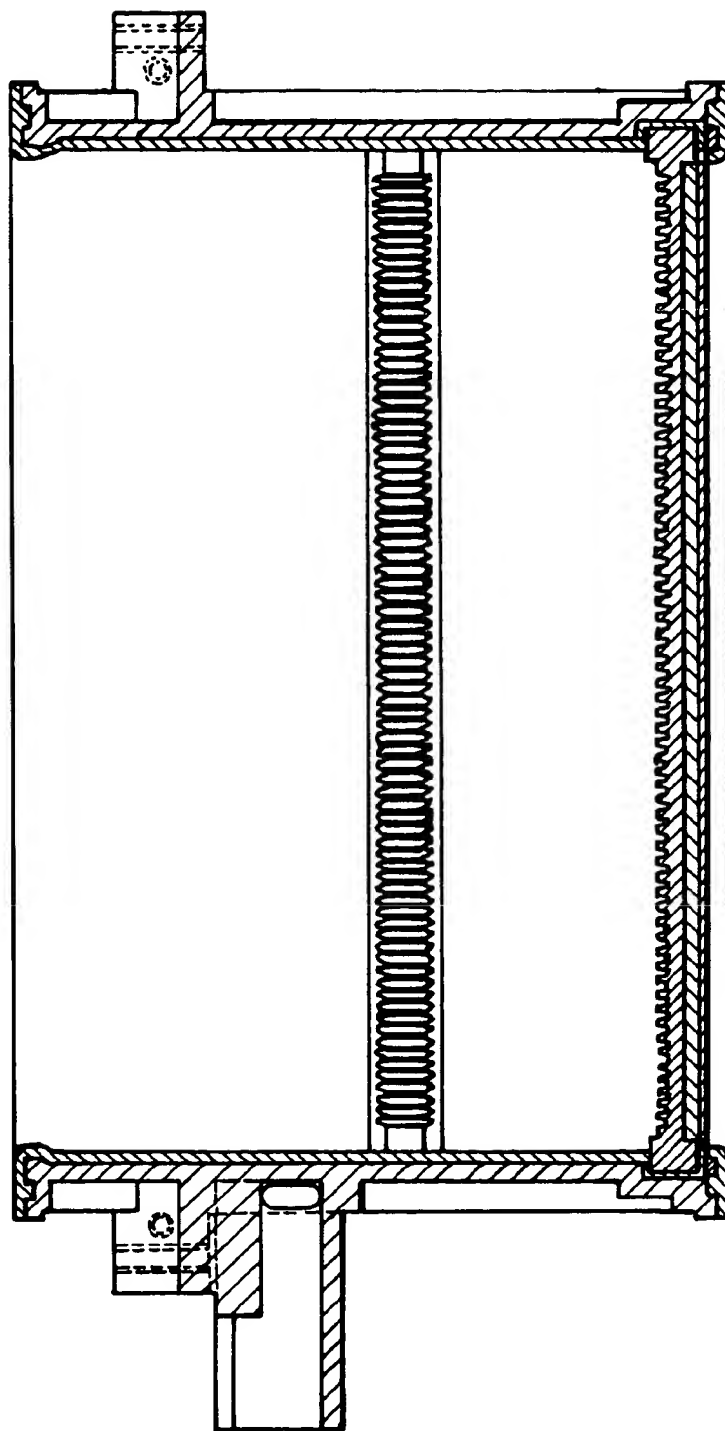


FIG. 5C



**FIG. 5D**

FIG. 6



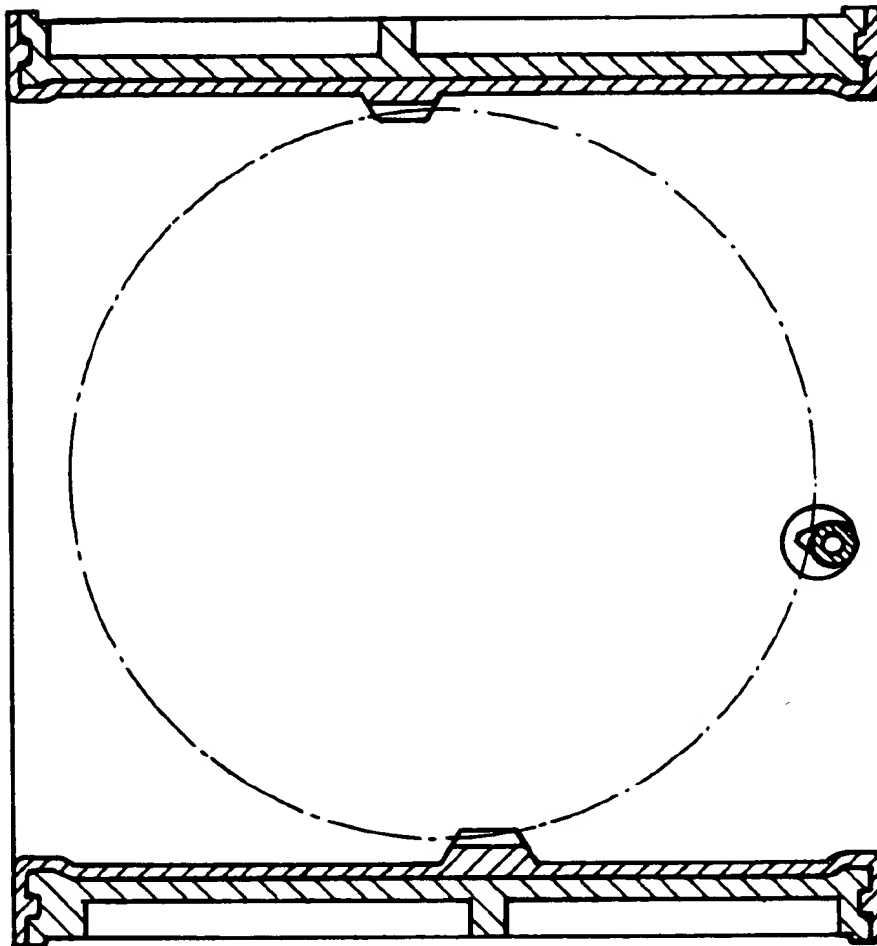


FIG. 7

## METHODS FOR TREATING SEMICONDUCTOR WAFERS

This application claims the benefit of U.S. Provisional Application Ser. No. 60/050,076 filed Jun. 13, 1997.

### FIELD OF THE INVENTION

The present invention relates to the field of treating (i.e., etching and/or cleaning) semiconductor wafers with a solution containing ammonium fluoride and control of the process used for preparing such a solution at its point of use.

### BACKGROUND OF THE INVENTION

Various solutions have been used to clean and etch semiconductor wafers. Recently, general cleaning solutions, and particularly solutions designed for oxide etching, have been prepared containing ammonium fluoride as the primary cleaning or etching compound. In such instances, the semiconductor processing unit is designed to store the already prepared ammonium fluoride solution, which is then used when needed by the semiconductor processor.

Such solutions have been referred to as buffered HF solutions and consist of a mixture of hydrogen fluoride (HF), which is a weak acid, and a salt of this acid, ammonium fluoride ( $\text{NH}_4\text{F}$ ). Initially this mixture was developed to buffer dilute HF so as to obtain a constant etch rate over an extended period of time (i.e., several days to weeks). Such solutions may be referred to as Buffered HF (BHF); the term BOE (Buffered Oxide Etch) is also used to refer to these solutions. Therefore, the appropriate solution (i.e., BHF or dHF) can be selected to optimize the specific etching and/or cleaning step to be performed.

It was discovered, however, that buffered hydrogen fluoride has slightly different properties than dilute HF, aside from the buffering, which can be used to a semiconductor processor's advantage in several occasions.

The major difference between BHF and dHF (dilute HF) is the different pH of the solutions. BHF has a pH of around 3 to 5, whereas dHF has a pH of around 1 to 2. Thus, the active species in the solutions is different.

The use of a BHF solution is attractive in some semiconductor processing applications because: (1) resist is more "stable in" to BHF than to dHF (dilute HF) as a result of BHF's higher pH; (2) BHF has different etch selectivity than dHF (e.g., BHF is used when the BPSG (borophosphosilicate glass) versus thermal oxide has to be lower than the selectivity obtained in dHF; or BHF can also obtain the opposite if formulated right (i.e., it can also offer much higher etch rates for BPSG than thermal oxide); (3) BHF offers higher oxide etch rates than dHF for the same fluoride concentration; (4) BHF also offers higher nitride etch rates; (5) BHF terminates the surface differently than dHF; and (6) the higher pH of the BHF may in certain cases offer an improved particle performance depending on the particular action of the zeta potential.

In conventional BHF techniques, the solution is premixed and then employed in a wet processing unit. There are various problems associated with the use of premixed BHF. For example, particle formation tends to be an issue; such particles may compromise the integrity of the final product. Etch uniformity is limited due to the high viscosity and surface tension of BHF, the high etch rate, and, in the case of a wet bench, the continuous etching during insertion or removal of the wafers from the processing tanks and into the rinse tank. Also, because premixed BHF is typically used for

an extended period of time, sometimes up to a week, there is the potential to introduce metallic impurities into the process liquids, which could again, compromise the integrity of the final product. Further, BHF tends to crystallize at temperatures below 16–17° C. which poses a problem for commercial transportation of the premixed chemical from various locations (i.e., supplier to water processing plant). Because premixed BHF has a high viscosity and surface tension, a surfactant is generally required to improve its wetting properties and to reduce particle formation. Finally, with premixed BHF, one is limited to the premixed ratio of  $\text{NH}_4\text{F}$  to HF, typically mixing ratios of 6:1, 7:1 or 10:1, limiting flexibility in processing. The use of premixed BHF also is expensive.

Although there are significant benefits to using BHF to treat electronic component precursors, there is a need to reduce the problems associated with premixed BHF. The present invention addresses these as well as other needs.

### SUMMARY OF THE INVENTION

The present invention provides improved methods for cleaning or etching semiconductor wafers, and particularly for oxide etching semiconductor wafers, using a cleaning/etching aqueous solution that contains ammonium fluoride ( $\text{NH}_4\text{F}$ ) and preferably also contains hydrogen fluoride (HF) (or hydrofluoric acid). Such a solution can also be referred to as a buffered HF solution (BHF) or a buffered oxide etch (BOE) solution. The methods of the present invention provide for the preparation of such a BHF solution directly at the point of use of the solution within the semiconductor processing area, or "fab" by mixing hydrofluoric acid with a base or by injecting them into a process vessel. Hydrofluoric acid and ammonium hydroxide may be used to formulate the solution. In such a way, the present invention provides great advantages to a semiconductor processor. One advantage is that the semiconductor processor can incorporate the methods of the present invention into its operation without significant retrofitting because the raw material reagents—aqueous solution of hydrogen fluoride (hydrofluoric acid) and aqueous solution of ammonium hydroxide—are already used for other processing steps; thus, the present invention allows the processor to eliminate an entire chemical reagent (premixed BHF) from the processing area. Another advantage is that the present methods may reduce problems with particles in the processing system. Additionally, the present invention may provide improved etch uniformity over conventional BHF techniques. A further advantage is that the present invention may provide improved purity for the BHF solution with a lower concentration of metallic impurities. Finally, the present invention allows any mixing ratio at point of use providing increased processing flexibility. The mixing ratio can be easily changed at any run.

By using a point of use BHF solution, it has been observed that the particle counts were generally negative at 0.16  $\mu\text{m}$ , typically something like -100 to -200. Further, using point of use BHF, etch uniformities of 2–3% can readily be obtained, even without optimization for etch uniformity. Problems of contamination with metallic impurities and crystallization are minimized, if not eliminated using point of use BHF. Coinjected BHF does not generally require the use of surfactants and it also allows one to deliver any mixing ratio of  $\text{NH}_4\text{F}$  to HF, which is beneficial because it provides for added flexibility in wet processing techniques allowing etch rate and selectivity to be optimized for a given semi-conductor process. Coinjected BHF is also more cost efficient because there is (1) no need for extra chemical lines



in the clean room because the individual chemicals are typically used in other wet processing steps; (2) no need for extra chemicals to be qualified and quality controlled, again, because the individual chemicals are typically used in other wet processing steps; and (3) no need for surfactant-chemical waste processing.

In one embodiment of the present invention, the method for treating semiconductor wafers with a solution containing ammonium fluoride, comprises the following steps. First, there is provided a source of ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and a source of hydrogen fluoride ( $\text{HF}$ ). Then an amount of ammonium hydroxide is transferred from the source of ammonium hydroxide to a treatment vessel and an amount of hydrogen fluoride is transferred from the source of hydrogen fluoride to the treatment vessel to prepare a treatment solution comprising ammonium fluoride ( $\text{NH}_4\text{F}$ ) and  $\text{HF}$ . A plurality of semiconductor wafers are contacted with the treatment solution to remove waste material from the semiconductor wafers.

It is preferred that in the resulting treatment solution the molar concentration of  $\text{NH}_4\text{F}$  is from about 0.02 to about 20 and the molar concentration of  $\text{HF}$  is from about 0.01 to about 30. Preferably  $\text{NH}_4\text{F}$  is 0.10–10 moles/liter and  $\text{HF}$  range is 0.10–20 moles/liter.

The treatment solution may be used for various reasons, such as oxide, nitride, or titanium (without limitation) etching the surfaces of semiconductor wafers, or general cleaning of the semiconductor wafers.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts the correlation between etch rate and fluoride concentration.

FIG. 2 depicts the relative (fractional of the total fluoride concentration) concentration of the different species in a BHF solution as a function of pH for a total fluoride concentration of 2 mole/l (corresponding to a 14:1 dilution of  $\text{H}_2\text{O}:\text{HF}$ ).

FIG. 3 depicts the relative concentration of the species in BHF as a function of pH for a total fluoride concentration of 0.14 mole/l.

FIG. 4 depicts the ratio of  $[\text{HF}_2^-]/[\text{HF}]$  as a function of the dilution of  $\text{H}_2\text{O}:\text{HF}$ .

FIG. 5 depicts CFM Technology's 8100 Full-Flow System, which is an example of a wet processing system that may be used for practicing the claimed invention.

FIG. 6 depicts a vessel area of the unit of FIG. 5 showing the slots where the electronic precursors are placed during treatment.

FIG. 7 depicts a wafer held in a vessel in the CFM Technology's Full-flow™ system.

#### DETAILED DESCRIPTION OF THE INVENTION

The terminology "reactive process liquid," "reactive chemical process liquid," "processing liquid," "chemical liquid," "active chemical," "reactive chemical process liquid," or "treatment solution," as used herein, refers to the reactive liquids that electronic component precursors are exposed to during their manufacture and perform some action on the surface electronic component precursors, as distinguished from a rinsing liquid such as DI water. These terms may be used interchangeably. When used in connection with the terminology "process liquid," "reactive" or "active" means, without limitation, a process liquid that has some activity in removing contamination such as particulate,

metallic impurities, or organic from the surface of the electronic component precursor, or has some activity in etching the surface of the electronic component precursor, or active in growing an oxide layer on the surface of the electronic component precursor. An example of such a reactive chemical process liquid is an aqueous solution of hydrofluoric acid ( $\text{HF}$ ), which may have a concentration greater than 1000:1 ( $\text{H}_2\text{O}:\text{HF}$ ).

The terminology "nonreactive chemical process liquid," as used herein, refers to a process liquid that does not necessarily have any activity in, for example, removing contaminants from the electronic component precursors, and may include rinse liquids.

The terminology "chemical treatment step," as used herein, refers to exposing the electronic component precursors to one reactive chemical process liquid.

The terminology "treating," as used herein, refers to some active step being performed on an electronic component precursors, such as cleaning or etching.

The terminology "wet processing treatment," as used herein, refers to exposing the electronic component precursors to one or a series of process liquids to, for example, clean or etch the surfaces of the electronic component precursors.

The terminology "rinsing liquid" or "rinse liquid," as used herein, refers to DI water or some other liquid that is used to rinse the electronic component precursors after exposure to a reactive chemical process liquid, as compared to treating them with a chemical. A rinse liquid may be DI water or a very dilute aqueous solution of a chemical (e.g., hydrochloric acid) to prevent, for example, metallic deposition on the surface of the electronic component precursors during rinsing (using very dilute solution of hydrochloric acid). Ozone is another additive used during rinsing. The chemical concentration in such rinsing liquids is minute; generally, the concentration is not greater than about 100 ppm. The primary goal of the rinsing liquid is to remove chemicals or reaction products from the surface of the electronic component precursors, and not to perform some "reactive" process to the surface(s) of the electronic component precursors.

The terminology "reaction chamber," as used herein, refers to vessels, full flow vessels or single tank systems, baths, wet benches and other reservoirs suitable for wet processing methodologies. This terminology is interchangeable with the terminology "treatment vessel."

As used herein, the terminology "full flow vessel," refers to a vessel that is closed to the environment and is employed in a "full flow method," or sometimes called one bath systems.

As used herein, the terminology "electronic component precursors" includes, without limitation, semiconductor wafers, flat panels, and other components used in the manufacture of electronic components (i.e., integrate circuits).

The methods of the invention are generally applicable to any wet processing equipment. Reaction chambers suitable for practicing the claimed invention include, without limitation, full flow vessels, single chambers, wet benches (baths), and spray cleaning systems. See, e.g., Chapter 1: Overview and Evolution of Semiconductor Wafer Contamination and Cleaning Technology by Werner Kern and Chapter 3: Aqueous Cleaning Processes by Don C. Burkman, Donald Deal, Donald C. Grant, and Charlie A. Peterson in Handbook of Semiconductor Wafer Cleaning Technology (edited by Werner Kern, Published by Noyes Publication Parkridge, N.J. 1993), and Wet Etch Cleaning by Hiroyuki Horiki and Takao Nakazawa in Ultraclean Technology

Handbook, Volume 1, (edited by Tadahiho Ohmi published by Marcel Dekker), the disclosures of which are herein incorporated by reference in their entirety. A particularly preferred wet processing system is CFM Technology's 8100 Full-Flow™ system.

Semiconductor fabrication is described generally, for example, in P. Gise et al., *Semiconductor and Integrated Circuit Fabrication Techniques* (Reston Publishing Co. Reston, Va. 1979), the disclosures of which are herein incorporated by reference in their entirety.

The reactive chemical process liquids suitable for practicing the invention include, without limitation, aqueous solutions of hydrochloric acid and buffers comprising the same, ammonium hydroxide and buffers comprising the same, hydrogen peroxide, sulfuric acid and buffers comprising the same, mixtures of sulfuric acid and ozone, hydrofluoric acid and buffers comprising the same, chromic acid and buffers comprising the same, phosphoric acid and buffers comprising the same, acetic acid and buffers comprising the same, nitric acid and buffers comprising the same, ammonium fluoride buffered hydrofluoric acid, ammonium hydroxide and buffers comprising the same, and hydrofluoric acid and buffers comprising the same, and combinations thereof. BHF can be used at anytime during a wet processing technique. The particular process liquids used, the equipment used, the exposure time, and the experimental conditions (i.e., temperature, concentration, and flow of the process liquid) will vary depending on the particular purpose of the particular wet processing methodology.

The reactive chemical process liquids may further contain additional additives such as surfactants, complexing or chelating agents, and corrosion inhibitors.

The nonreactive chemical process liquids suitable for practicing the invention include, without limitation, deionized water or very dilute solutions of deionized water and/or chemical. Examples of such chemicals include, without limitation, hydrochloric acid, hydrofluoric acid, nitric acid, hydrogen peroxide, ozone, and surfactant.

After chemical treatment, the electronic component precursors may be dried using any method known to those skilled in the art.

The methods of the invention may be used for etching or cleaning the surfaces of semiconductor wafers to remove any unwanted layer or part thereof from the silicon surface, such as an oxide layer, a nitride layer, an aluminum layer, a titanium layer (without limitation). The present invention may also be used in controlled oxide etching.

The present invention provides methods for using a buffered, aqueous hydrogen fluoride (BHF) solution that contains hydrogen fluoride (HF), which is a weak acid, and a salt of this acid, ammonium fluoride ( $\text{NH}_4\text{F}$ ). This BHF solution is used, inter alia, to clean or etch electronic component precursors such as semiconductor wafers, flat panels, and other electronic component precursors. Hereinafter, the invention will be described with respect to cleaning or etching semiconductor wafers as representative of electronic component precursors. The cleaning or etching step accomplished by such BHF solutions can include general cleaning of the wafers, and is particularly applicable to oxide etching of the wafers. The invention, however, is not limited to such cleaning.

In accordance with the present invention, the BHF solution is prepared directly at the site of its end use. The BHF can be prepared in a mixing tank from its individual components and then transferred to a treatment vessel which is in fluid communication with the mixing tank, or the BHF

can be prepared in the treatment vessel itself. In such a way, the BHF solution can be prepared within the processing room of the semiconductor processor with chemical reagents typically used in other processing aspects of such wafers. This allows for the minimization of raw chemical reagents that need to be stored in the processing area, or "fab," and thereby streamlines the processing area.

A typical processing area for treating semiconductor wafers will have storage tanks for chemical reagents, such as ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and hydrofluoric acid (HF). These reagents are typically stored in their concentrated form. For  $\text{NH}_4\text{OH}$ , a concentrated solution will typically be about 29% wt. aqueous solution; for HF, a concentrated solution will typically be about 49% wt. aqueous solution. These solutions can also be kept in a diluted form, with the lowest concentration of the  $\text{NH}_4\text{OH}$  solution being about 400 parts water:1 part  $\text{NH}_4\text{OH}$  and the same lowest concentration for the HF solution.

In accordance with the methods of the present invention, a BHF process solution is prepared directly within the processing area at the point of its use to clean and/or etch the semiconductor wafers. In one embodiment, there is prepared a BHF process solution within a treatment vessel. The treatment vessel is in liquid communication with the storage tanks for the  $\text{NH}_4\text{OH}$  and for the HF solutions. A control valve and a control pump can be used as processing equipment between these storage tanks and the treatment vessel. In such a way, a processing control system, such as a personal computer, can be used as a means to control and monitor the addition rates of each solution, the  $\text{NH}_4\text{OH}$  and for the HF solutions, into the treatment vessel to prepare the processing solution.

The BHF process solution will be prepared by mixing together a selected quantity of the  $\text{NH}_4\text{OH}$  aqueous solution and a selected quantity of the HF aqueous solution. The reaction of these two compounds will form  $\text{NH}_4\text{F}$ . The two reactant species are combined in a ratio such that there is a molar excess of HF to produce a final BHF process solution that contains both  $\text{NH}_4\text{F}$  and HF. It is preferred that the BHF process solution contain a molar concentration (moles/liter of solution) of  $\text{NH}_4\text{F}$  in the range of from about 0.02 to about 20, and that it also contain a molar concentration of HF in the range of from about 0.01 to about 30. Preferably  $\text{NH}_4\text{F}$  is 0.10–10 moles/liter and HF range is 0.10–20 moles/liter. The BHF process solution can also be prepared without an excess of HF, such that there is no detectable amount of HF in the BHF process solution, although it is preferred to have an excess of HF present.

After the  $\text{NH}_4\text{OH}$  solution and the HF solutions have been transferred into the treatment vessel to form the BHF process solution, the equipment used to transfer those reagents, e.g., any pumps and/or valves, can be shut down. The BHF process solution is now in a form to be used at the point of its end use to clean and/or etch silicon wafers. This step can be accomplished by any of the variously known contacting steps. One such method is to immerse the wafers into the BHF process solution within the treatment vessel. Another method is to flow the BHF process solution over the wafers or to spray the process solution onto the wafers.

The temperature of the BHF process solution can be maintained between about 3° C. and about 90° C., preferably between about 15° C. and 70° C., most preferably between 20° C.–40° C.

The process of mixing the separate  $\text{NH}_4\text{OH}$  and the HF solutions to form the BHF process solution can be automated to an extent. That is, the known concentrations of

these solutions can be entered into a computer and a program can then be used to control the addition rate of each solution to produce the desired concentration of  $\text{NH}_4\text{F}$  and  $\text{HF}$  in the final BHF process solution.

The BHF process solution of the present invention is preferably used in oxide etching processing steps to remove silicon oxides from the surfaces of semiconductor wafers. The unwanted oxides include PBSPG oxides and thermal oxides.

The preparation of the BHF process solution in accordance with the present invention at the point of its use within the processing area provides many benefits to the prior technique of storing a solution of  $\text{NH}_4\text{F}$  in the processing area and transferring that solution directly into the treatment vessel to be used as the process solution. For instance, use of the present methods may significantly decrease the accumulation of particles in the processing system. Also, the methods of the present invention may improve the uniformity of the etching process. In accordance with the present invention, any mixing ratio is possible between the  $\text{HF}$  solution and the  $\text{NH}_4\text{OH}$  solution. Further, the process of the present invention results in the simplification of the processing area because the space and equipment necessary to deal with a separate  $\text{NH}_4\text{F}$  solution are saved.

Without departing from the spirit of the invention, the BHF solution can be formulated at point of use by mixing hydrofluoric acid with a base, with ammonium hydroxide being the preferred base. Other bases suitable for practicing the invention include, without limitation, tetramethyl ammonium hydroxide.

The following examples are for illustrative purposes and are not intended to limit the invention.

## EXAMPLES

### Example 1

#### Experimental Determination of Co-injected BHF Rates and Selectivity

##### 1. Experimental design

In a first experimental series of 23 etching experiments thermal oxide and silicon nitride wafers were used to scan the entire dynamic range of mixing of  $\text{NH}_4\text{OH}$  and  $\text{HF}$ . The mixed or co-injected  $\text{HF}$  was varied such that the excess amount of  $\text{HF}$  (more  $\text{HF}$  than the amount required just to form  $\text{NH}_4\text{F}$ ) for every  $\text{NH}_4\text{OH}$  mixing amount (or injection) spanned between 10% and 100%.

In a second experimental series, 8 etching experiments were chosen from these 23 previous experiments to investigate the BHF etching selectivity of thermal oxide etching versus BPSG and TEOS oxide.

Both etch rate and selectivity experiments were performed in a CFM technology 8100 Full-Flow™ System.

##### 2. Dynamic range

The dynamic range for injection of  $\text{NH}_4\text{OH}$  ranges from 400:1 to 3:1 in a CFM Technologies 8100 Full-Flow™ system. In the presence of excess  $\text{HF}$ , every mole of  $\text{NH}_4\text{OH}$  will react together with  $\text{HF}$  to form one mole of  $\text{NH}_4\text{F}$  and therefore the dynamic range of  $\text{NH}_4\text{F}$  in CFM Technologies 8100 Full-Flow™ system is 0.0426 mole/l to 5.686 mole/l. If  $\text{NH}_4\text{F}$  would be supplied in a 40%-w solution, then this would correspond to a dilution of 254:1 and 1.89:1 dilution of  $\text{H}_2\text{O}:\text{NH}_4\text{F}$  (40% w). Or alternatively said, the dynamic range of the CFM Full-Flow corresponds to  $\text{NH}_4\text{F}$  or  $\text{NH}_4\text{OH}$  concentrations of between 0.15%-w and 21%-w.

This dynamic range was explored while adjusting the excess  $\text{HF}$  concentration from 10% to 100% of the  $\text{NH}_4\text{F}$  concentration (excess  $\text{HF}$  is varied from 10% to 100% of  $\text{NH}_4\text{F}$  molar concentration).

## 3. Experiments

### a. Design of experimental conditions

The experimental design of the first series of experiments is shown in Table 1. In this table, the injected ratios are shown with respect to a basis for  $\text{HF}$  (i.e.,  $\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{HF}$ ). The  $\text{NH}_4\text{F}$  spans the entire dynamic range of the CFM 8100 Full-Flow™ (400:1 to 10:1). The  $[\text{HF}]/[\text{NH}_4\text{F}]$  ratio varies between 10% and 100%.

In a second set of experiments 8 etching experiments were chosen to run with different types of oxides. In each run 5 wafers were used: 1 native oxide wafer for particle addition test, and 1 thermal oxide wafer, 1 BPSG wafer, one TEOS wafer, and 1 silicon nitride wafer. The last four wafers were tested for etch uniformity and selectivity.

### 4. Results

The recipe for BHF in a CFM Full-Flow™ 8100 looks similar to an SC1 ( $\text{H}_2\text{O}_2$ ,  $\text{NH}_4\text{OH}$ , and  $\text{H}_2\text{O}$ ) or SC2 ( $\text{H}_2\text{O}_2$ ,  $\text{HCl}$ , and  $\text{H}_2\text{O}$ ) step. The step is called  $\text{HF}/\text{NH}_4\text{OH}$ . An example of a set of reaction conditions that may be used for a run in a CFM 8100 Full-Flow™ System is as follows:

Condition flow	20 gpm
Condition temp	35° C.
Inject Time	60.0 Secs
Soak Time	60.0 Secs
Ratio Water	100
Ratio HF	0.77
Ratio $\text{NH}_4\text{OH}$	1
Megasonics ON	0.0 Secs
Megasonics OFF	0.0 Secs

### a. Conversion Calculations

From the volumetric ratio of  $\text{NH}_4\text{OH}$  and  $\text{HF}$  to  $\text{H}_2\text{O}$  in the recipe, the following items can be calculated:

If recipe input (volumetric ratios):

$$\begin{aligned} \text{H}_2\text{O} &= a \\ \text{NH}_4\text{OH} &= b \\ \text{HF} &= c \end{aligned}$$

Then

$$[\text{HF}] \text{ concentration injected in mole/l as } \text{HF} = c / a * 1000 * 1.18 * (49/100) / 20.006 * (a / (a + b - 1 - c))$$

In this formula it is assumed that the specific density of  $\text{HF}$  in a 49%-w solution is 1.18 and that the  $\text{HF}$  is supplied to the injection tubes in a 49% concentration by weight of  $\text{HF}$ . Further it is assumed that the molecular weight of  $\text{HF}$  is 20.006 g/mole. The  $[\text{NH}_4\text{OH}]$  can be determined by

$$[\text{NH}_4\text{OH}] \text{ injected in mole/liter} = b / a * 0.9 * (29/100) * 1000 / 17 * a / (a + b + c).$$

In this formula it is assumed that the specific density of  $\text{NH}_4\text{OH}$  in a 29% solution is a 0.9 and that the  $\text{NH}_4\text{OH}$  is supplied to the injection tubes in a 29% concentration by weight of  $\text{NH}_3$ . Further it is assumed that the molecular weight of  $\text{NH}_3$  is 17 g/mole.

### b. Discussion and further conversions

The injected  $\text{HF}$  and  $\text{NH}_4\text{OH}$  will form  $\text{HF}$  and  $\text{NH}_4\text{F}$ . More specifically, this  $\text{HF}$  and  $\text{NH}_4\text{F}$  will further form  $\text{HF}$ ,  $\text{HF}_2^-$ ,  $\text{F}^-$ ,  $\text{NH}_4$  and higher polymers of  $\text{HF}$  such as  $(\text{HF})_2$ . Alternatively the same concentration of species in the vessel could be generated by injecting  $\text{HF}$  and  $\text{NH}_4\text{F}$  directly through the injection tubes. The amount of  $\text{HF}$  and  $\text{NH}_4\text{F}$  that would be required in the injection tubes (hypothetically, since  $\text{HF}$  and  $\text{NH}_4\text{OH}$  are really injected) to achieve equivalent concentration of active species in the vessel can be calculated. Equivalent amounts of  $[\text{HF}]$  and  $[\text{NH}_4\text{F}]$  hypothetically injected (if injecting  $\text{HF}$  and  $\text{NH}_4\text{F}$  instead of  $\text{HF}$  and  $\text{NH}_4\text{OH}$ ):

$$[\text{NH}_4\text{F}] \text{ in } \text{NH}_4\text{F}-\text{HF} \text{ scheme} = [\text{NH}_4\text{OH}] \text{ in } \text{NH}_4\text{OH}-\text{HF} \text{ scheme}$$

[HF] in  $\text{NH}_4\text{F}$ —HF scheme=[HF]—[ $\text{NH}_4\text{OH}$ ] in  $\text{NH}_4\text{OH}$ —HF scheme

Therefore, the ratio of [HF]/[ $\text{NH}_4\text{F}$ ] is:

$$[\text{H F}]/[\text{NH}_4\text{F}]=([\text{H}_4\text{F}]-[\text{NH}_4\text{OH}])/[\text{NH}_4\text{OH}]$$

C. Conversion of HF/ $\text{NH}_4\text{F}$  (molar to  $\text{NH}_4\text{OH}$ /HF (volumetric))

To convert a [HF]/[ $\text{NH}_4\text{F}$ ] ratio into a volumetric ratio of  $\text{NH}_4\text{OH}$  (29%)/HF (49%) the following formula can be used:

$$\text{NH}_4\text{OH (29\%)/HF (49\%)}=1.8825/([\text{HF}]/[\text{NH}_4\text{F}]+1) \text{ for } [\text{HF}]/[\text{NH}_4\text{F}]=0, \text{ this gives } \text{NH}_4\text{OH}/\text{HF}=1.8825.$$

Therefore, the maximum volumetric ratio of  $\text{NH}_4\text{OH}$  to HF injection is 1.8825.

#### 5. Measurements

##### a. On the wafers

Etched oxide (25 points, 6 mm edge exclusion), etched nitride (25 points, 6 mm edge exclusion), particle removal (>0.16  $\mu\text{m}$ , 5 mm edge exclusion) on oxide wafers, nitride wafers, and test wafers (native oxide). Particles were mea-

sured using the Tencor Surfscan 6220 in the CFM Apps Lab. The film thickness was measured using the Rudolph FE VII-D at Rudolph Technologies in Flanders, N.J.

##### b. On the tool

D1 flow, actual volumes of chemicals injected (versus recipe volumes), temperature, conductivity at the end of the injection. Three wafers were used for each run. One nitride wafer was put into slot #22, the thermal oxide wafer was put into slot #32 and the test wafer was put into slot #42 (the slots are as depicted in FIG. 7).

##### 6. Results of 1st and 2nd set of experiments

Since  $\text{NH}_4\text{F}$  is made by mixing  $\text{NH}_4\text{OH}$  and HF the data can be represented as a function of  $\text{NH}_4\text{OH}$  and HF as done in Table 1. The dilution of HF with respect to  $\text{H}_2\text{O}$  is given on the vertical axis and the ratio of  $\text{NH}_4\text{OH}$  to HF is given on the other axis. A ratio of  $\text{NH}_4\text{OH}$  to HF of 1.8825 delivers a perfect  $\text{NH}_4\text{F}$  solution (ie., no excess HF). Higher ratios will form  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{F}$  instead of HF and  $\text{NH}_4\text{F}$ .

TABLE 1

Thermal oxide etch rate at 40° C. in A/min. Some runs were run at 35° C. The runs at 35° C. are printed in smaller characters. The data is now presented as a function of  $\text{NH}_4\text{OH}$  and HF. The  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{O}$  is giving in volumetric ratios compared to 1 part HF. Thus, the volumetric ratio is presented as  $\text{H}_2\text{O}:\text{NH}_4\text{OH}:1$ , where 1 is HF. The data for 0  $\text{NH}_4\text{OH}$  is the standard CFM data for dilute HF solutions.

$\text{NH}_4\text{OH}:\text{H}_2\text{O}:\text{HF}$	0	0.85	0.70	0.73	0.74	0.75	0.76	0.78	0.81	0.84
500.1	10									
400.1										
357.1										
333.1										
294.1					18					
270.1							14			
250.1				16						
232.1				20				17		
204.1										
200.1	25									
189.1			26							
182.1									27	
175.1		32								
154.1										32
150.1	33									
147.1										
127.1										35C/36
125.1	40									
116.1										
111.1	48					35C/46				
101.1										
100.1	50									
98.1										
92.1						68				
90.1	5									
89.1										
88.1										
85.1										
80.1	82									
74.1										
70.1	71									
68.1										
65.1										
63.1										
60.1	83									
53.1										
50.1	99									
48.1										
40.1	123									
37.1										
35.1	140									
29.1										
23.1										
16.1										
13.1										
11.1										

TABLE 1-continued

Thermal oxide etch rate at 40° C. in A/min. Some runs were run at 35° C. The runs at 35° C. are printed in smaller characters. The data is now presented as a function of NH<sub>4</sub>OH and HF. The NH<sub>4</sub>OH and H<sub>2</sub>O is giving in volumetric ratios compared to 1 part HF. Thus, the volumetric ratio is presented as H<sub>2</sub>O:NH<sub>4</sub>OH:1, where 1 is HF. The data for 0 NH<sub>4</sub>OH is the standard CFM data for dilute HF solutions.

NH <sub>4</sub> OH H <sub>2</sub> O:HF	0.97	0.99	1.1	1.5	1.7	1.6	1.88	2.0	2.1	2.4
500.1										
400.1		7								
357.1										
333.1										
294.1										
270.1										
250.1										
232.1										
204.1										
200.1										
189.1										
182.1										
175.1										
154.1										
150.1										
147.1	35C/21									
127.1										
125.1										
116.1			35C/21							
111.1										
101.1				19						
100.1										
98.1										
92.1										
90.1										
89.1										
88.1										
85.1										
80.1										
74.1										
70.1										
68.1										
65.1										
63.1		156								
60.1										
53.1										
50.1										2 (Si etched)
48.1									129 (Si etched)	
40.1										
37.1		411(?)	247			83				3 (Si etched)
35.1										
29.1									he)	3 (Si etched)
23.1						263		37		3 (Si etched)
16.1		>840			>353	404				
13.1				>528						
11.1										

In the literature, H. Kikuyama, N. Miki, K. Saka, J. Takano, I. Kawanabe, M. Miyashita and T. Ohmi, IEEE Trans. On Semic. Manuf., Vol.4, no. 1, 26 (1991), it is reported that the highest etch rate is obtained for equal molar ratios of HF and NH<sub>4</sub>F. In terms of volumetric ratios of NH<sub>4</sub>OH and HF, this corresponds to a volumetric ratio of NH<sub>4</sub>OH/HF=0.94.

If the etch data for mixed solutions of NH<sub>4</sub>OH and HF for a ratio range of 1:0.86 to 1:1.2 are plotted together with the etch data for dilute HF on a graph versus the HF dilution, FIG. 1 results. FIG. 1 illustrates that the influence of the [NH<sub>4</sub>OH] on the etch rate is increasingly important for dilutions of 100:1 and lower. At a dilution of 100:1, the etch rate in BHF is about 20% higher, at a dilution of 70:1, the etch rate in BHF is about 50% higher and at a dilution of 63:1, the etch rate in BHF is about 100% faster than in dHF solutions with the same HF concentration. It seems that for dilutions higher than 100:1 the etch rate does not depend

greatly on the NH<sub>4</sub>OH concentration. These results agree very well with theory.

In BHF, there are following species present: H<sup>+</sup>, OH<sup>-</sup>, F<sup>-</sup>, HF<sub>2</sub><sup>-</sup>, HF and (HF)<sub>2</sub>. In dilute HF, the primary etchants are the undissociated HF molecule and the (HF)<sub>2</sub> dimer acting as the etchant. In BHF, HF<sub>2</sub> also etches the oxide. HF<sub>2</sub><sup>2-</sup> etches the oxide roughly 4 times faster than (HF)<sub>2</sub> and/or HF. The presence of HF<sub>2</sub> in the solution is strongly dependent on the pH of the solution.

At pH values between 3 and 5, the [HF<sub>2</sub><sup>-</sup>] concentration is much higher than the (HF) or (HF)<sub>2</sub> concentration, as shown in FIG. 2. However, this situation changes drastically for dilute solutions. The same graph is shown in FIG. 3 for the case of a 200:1 solution, corresponding to a molar concentration of 0.14 mole/l. In FIG. 3, the [HF<sub>2</sub><sup>-</sup>] concentration still goes through a maximum for pH values between 3 and 5, but the [HF<sub>2</sub><sup>-</sup>] concentration is always much lower

than the  $[HF]$  concentration. The ratio of  $[HF_2^-]$  versus  $[HF]$  can be calculated as a function of the dilution for a fixed pH value.

For a pH value of 3.6 the ratio of  $[HF_2^-]$  versus  $[HF]$  is shown in FIG. 4. The concentration of  $HF_2^-$  only becomes significant for dilutions less than a 100:1, illustrating why the addition of  $NH_4OH$  to  $HF$  only increases the etch rate for dilutions less than 100:1. Even though the addition of  $NH_4OH$  to  $HF$  for more dilute solutions does not alter the etch rate, it will still modify the pH which is important in patterned etches, where higher pH values are less aggressive to the resist. Additionally, there may be a slightly different surface termination depending on the pH, since there will be more  $F^-$  in the solution. Even though  $F^-$  does not etch  $SiO_2$ , it can still interact with  $Si$ . Finally, the addition of  $NH_4OH$  may affect particle formation since different pH values may result in improved particle performance depending on the action of the zeta potential between the particles and the wafer surface.

#### Example 2

##### BHF and CFM Technologies FULL-FLOW System

BHF can be made by mixing  $NH_4OH$  and  $HF$ , since  $NH_4OH$  and  $HF$  mixed will give  $NH_4F$ . If an over concentration of  $HF$  is used, then one obtains  $NH_4F$  and  $HF$ . In the CFM Full-Flow™ system, new software was developed to co-inject  $NH_4OH$  and  $HF$  to obtain BHF. Traditionally in mixtures of  $NH_4F$  and  $HF$ , ratios of 6:1 or 7:1 ( $NH_4F:HF$ ) are most popular, meaning volume ratios of  $NH_4F$  and  $HF$  and where  $NH_4F$  is delivered in a 40%-w solution and  $HF$  is delivered in a 49%-w solutions. However, concentrations as high as 20:1 are also used in the industry. The 6:1 volumetric ratio of  $NH_4F:HF$  actually corresponds to a molar ratio of 2.65:1. This can be achieved roughly by a volumetric ratio of 1:1 of co-injected  $NH_4OH$  and  $HF$  if the  $NH_4OH$  is delivered in a 29%-w solution and the  $HF$  is delivered in a 49%-w solution.

Indeed, in a 1:1 solution, there are 24.5 mole/l  $HF$  and 17 mole/l  $NH_4OH$ . The 17 mole/l  $NH_4OH$  together with 17 mole/l  $HF$  will form  $NH_4F$  and leave 7.5 mole/l  $HF$  excess. This gives a molar ratio of  $17:7.5=2.3:1$   $NH_4F:HF$ , close to the molar ratio in a 6:1 solution, which is 2.65:1.

This shows that co-injection of  $HF$  and  $NH_4OH$  in the CFM Full-Flow™ will require similar volumes of  $HF$  and  $NH_4OH$  to be injected, which is very advantageous, since now similar hardware can be used to inject both chemicals into the process vessel (reaction chamber).

What is claimed is:

1. A method for treating electronic component precursors with a solution containing ammonium fluoride, comprising the steps of:

- (a) providing a source of ammonium hydroxide ( $NH_4OH$ ) and a source of hydrogen fluoride ( $HF$ );
- (b) transferring an amount of ammonium hydroxide from the source of ammonium hydroxide to a treatment

vessel and transferring an amount of hydrogen fluoride from the source of hydrogen fluoride to the treatment vessel to prepare a treatment solution comprising ammonium fluoride ( $NH_4F$ ); and

(c) contacting a plurality of electronic component precursors with the treatment solution in the treatment vessel to remove waste material from the electronic component precursors.

2. The method of claim 1 wherein said electronic component precursors are semiconductor wafers.

3. The method of claim 1 wherein said source of ammonium hydroxide is selected from the group consisting of ammonium hydroxide and buffers thereof.

4. The method of claim 1 wherein said source of hydrogen fluoride is selected from the group consisting of hydrogen fluoridic acid and buffers thereof.

5. The method of claim 1 wherein said treatment solution further comprises an additive selected from the group consisting of surfactants, complexing agents, or corrosion inhibitors.

6. A method for treating electronic component precursors with a cleaning solution containing ammonium fluoride, comprising the steps of:

(a) providing a source of ammonium hydroxide ( $NH_4OH$ ) and a source of hydrogen fluoride ( $HF$ );

(b) transferring an amount of ammonium hydroxide from the source of ammonium hydroxide to a treatment vessel and transferring an amount of hydrogen fluoride from the source of hydrogen fluoride to the treatment vessel to prepare a treatment solution comprising ammonium fluoride ( $NH_4F$ ) and hydrogen fluoride, where the molar concentration of ammonium fluoride is from about 0.02 to about 15 and the molar concentration of hydrogen fluoride is from about 0.01 to about 30 in the treatment solution; and

(c) contacting a plurality of electronic component precursors with the treatment solution in the treatment vessel to remove waste material from the electronic component precursors.

7. The method of claim 6 wherein said electronic component precursors are semiconductor wafers.

8. The method of claim 6 wherein said source of ammonium hydroxide is selected from the group consisting of ammonium hydroxide and buffers thereof.

9. The method of claim 6 wherein said source of hydrogen fluoride is selected from the group consisting of hydrogen fluoridic acid and buffers thereof.

10. The method of claim 6 wherein said treatment solution further comprises an additive selected from the group consisting of surfactants, complexing agents, or corrosion inhibitors.

\* \* \* \* \*

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 5,972,123  
DATED : October 26, 1999  
INVENTOR(S) : Verhaverbeke

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page,

Item [56] insert the following:

**References Cited**

**U.S. PATENT DOCUMENTS**

5,306,400	5/3/94	Chen
5,447,890	9/5/95	Kato et al
4,171,242	10/16/79	Liu
4,545,918	10/8/85	Pralus
4,778,532	10/18/88	McConnell et al
4,795,582	01/03/89	Ohmi et al.
4,917,123	04/17/90	McConnell et al.

Column 7,

Line 27, please delete "hydrfluroic" and insert -- hydrofluoric -- therefor;

Line 27, please delete "hydrooxiude" and insert -- hydroxide -- therefor;

Line 30, please delete "hydrtoxide" and insert -- hydroxide -- therefor;

Line 29, please delete "tetramethly" and insert -- tetramethyl -- therefor;

Column 9,

Line 4, please delete "[H F]/[NH4F]=([H4F]-[NH4OH])/[NH4OH]" and insert -- [HF]/[NH4F]=[HF]-[NH4OH])/[NH4OH] -- therefor;

Column 10,

Line 17, please delete "ie.," and insert -- i.e., -- therefor;

Column 11 & 12,

Table 1- continued, header row, please delete "1.6" and insert -- 1.8 -- therefor;

UNITED STATES PATENT AND TRADEMARK OFFICE  
**CERTIFICATE OF CORRECTION**

PATENT NO. : 5,972,123  
DATED : October 26, 1999  
INVENTOR(S) : Verhaverbeke

Page 2 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

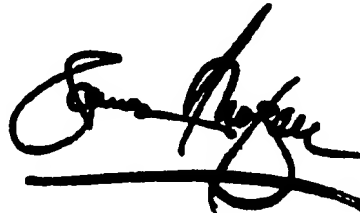
Column 13,

Line 39, please delete "17 mole/l" and insert -- 17 mole/l -- therefor.

Signed and Sealed this

Twenty-eighth Day of May, 2002

Attest:

A handwritten signature in black ink, appearing to read "James E. Rogan", with a horizontal line drawn underneath it.

Attesting Officer

JAMES E. ROGAN  
*Director of the United States Patent and Trademark Office*





US006242331B1

(12) **United States Patent**  
**Chu et al.**

(10) **Patent No.:** **US 6,242,331 B1**  
(45) **Date of Patent:** **Jun. 5, 2001**

(54) **METHOD TO REDUCE DEVICE CONTACT RESISTANCE USING A HYDROGEN PEROXIDE TREATMENT**

(75) Inventors: **Cheng-Yu Chu; Te-Fu Tseng**, both of Hsin-Chu; **Chai-Der Chang, Chia-Yi; Chi-Hung Liao**, Taipei, all of (TW)

(73) Assignee: **Taiwan Semiconductor Manufacturing Company, Hsin-Chu (TW)**

(\*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/467,129**

(22) Filed: **Dec. 20, 1999**

(51) Int. Cl.<sup>7</sup> ..... **H01L 21/3205**

(52) U.S. Cl. .... **438/586; 438/637; 438/677; 438/756**

(58) Field of Search ..... **438/637, 677, 438/756, 586, 624, 595; 134/4**

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

4,752,505	6/1988	Arac	427/307
5,229,334	7/1993	Kato	437/239
5,308,400	5/1994	Chen	134/2
5,486,266	1/1996	Tsai et al.	156/657.1
5,626,716 *	5/1997	Bosch et al.	438/723
5,670,019	9/1997	Huang	156/643.1
5,801,096	9/1998	Lee et al.	438/636

5,885,865 *	3/1999	Liang et al.	438/253
5,885,895 *	3/1999	Liu et al.	438/637
5,908,509 *	6/1999	Olesen et al.	134/1.3
5,939,333 *	8/1999	Hurley et al.	438/241
5,972,123 *	10/1999	Verhaverbeke	134/3
6,046,103 *	4/2000	Thei et al.	438/624

\* cited by examiner

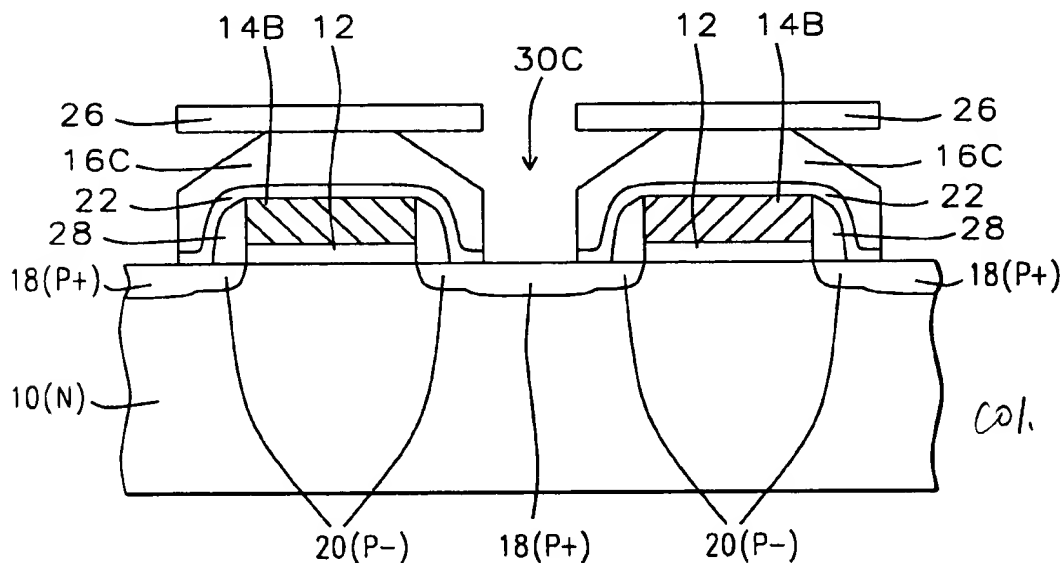
*Primary Examiner*—T. N. Quach

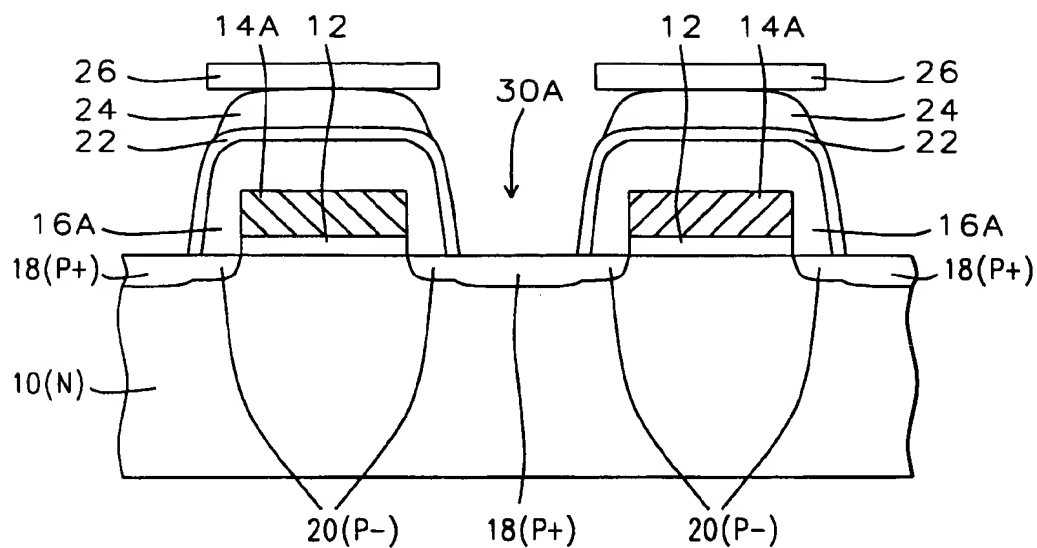
(74) *Attorney, Agent, or Firm*—George O. Saile; Stephen B. Ackema

(57) **ABSTRACT**

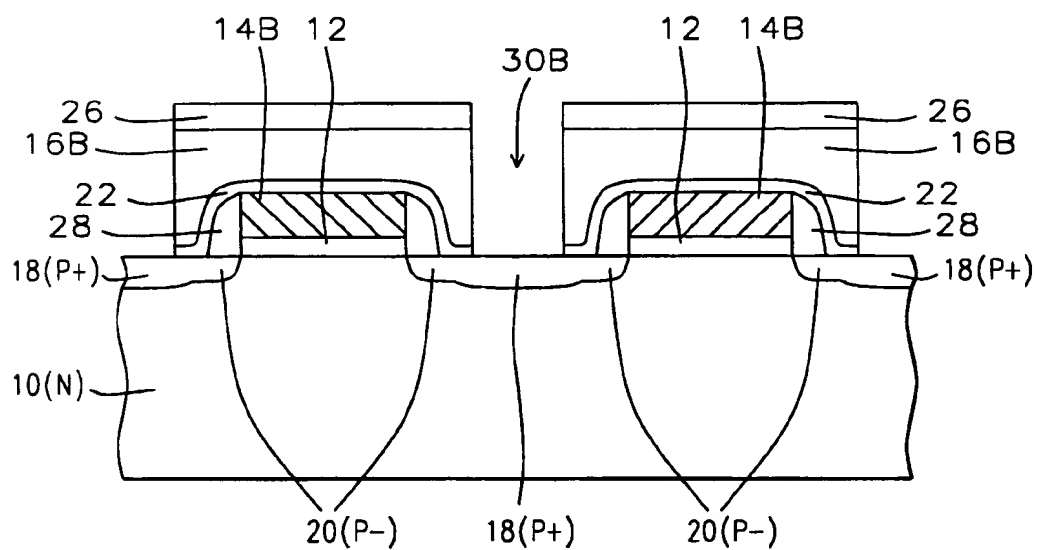
A method for developing a semiconductor device low resistance electrical contact is described. In this process a gate oxide layer followed by a polysilicon layer is deposited on the semiconductor substrate in proximity to the device contact area. It is subsequently patterned with photoresist and etched to produce the desired gate structure. This is followed by a deposited layer of silicon dioxide or silicon nitride (SIN) which is appropriately patterned and etched to form gate isolation spacers. Then a nominal 300 Å layer of silicon nitride (SIN) is deposited followed by a layer of tetraethyl orthosilicate (TEOS) or borophosphosilicate glass (BPSG). The contact area is defined by photolithography, and the passivation layers are etched either by a dry etch such as a RIE process, or a combination of a wet BOE process followed by a dry etch, to form the metal contact holes. Prior to sputtering the contact metal, the contact area is cleaned with a 30 second dip in a BOE solution, followed by a Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) dip. This H<sub>2</sub>O<sub>2</sub> cleaning step enables lower device contact resistance for the P+ contact areas.

**32 Claims, 2 Drawing Sheets**

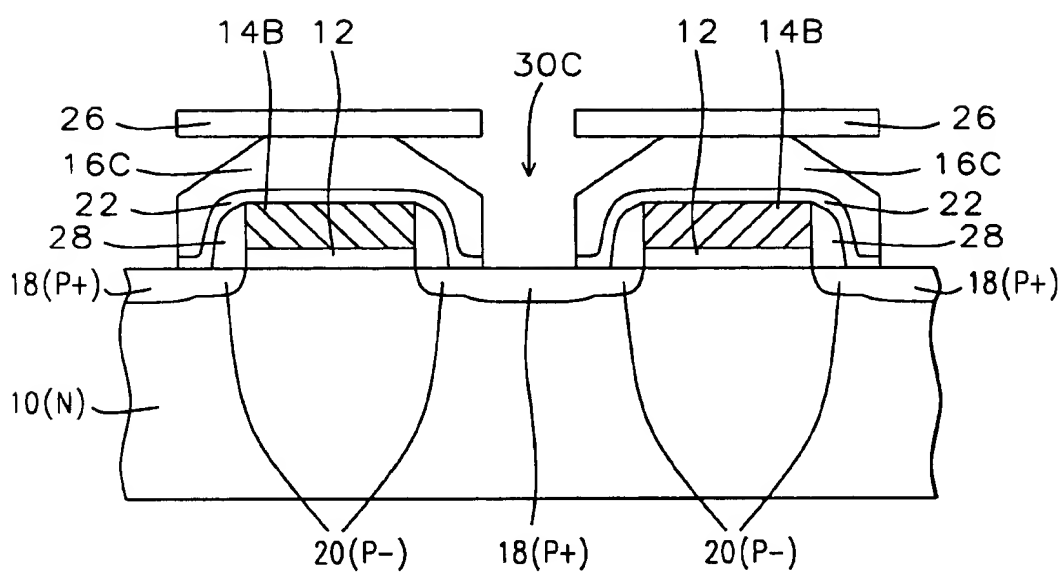




*FIG. 1 - Prior Art*



*FIG. 2*

*FIG. 3*

1

# METHOD TO REDUCE DEVICE CONTACT RESISTANCE USING A HYDROGEN PEROXIDE TREATMENT

## BACKGROUND OF THE INVENTION

### (1) Field of the Invention

The present invention relates to a method for semiconductor manufacturing and more specifically the cleaning of the surface of a semiconductor device prior to the deposition of the contact metallization layer, and particularly, to a method utilizing a hydrogen peroxide cleaning treatment to remove traces of contaminants in the metal contact area prior to the deposition of the contact metal.

### (2) Description of Prior Art

As circuit density and therefore device density increases, metal contact dimensions have to be decreased accordingly to minimize the contact area as part of the total chip area. Contact resistance is normally inverse to contact size, that is the smaller the contact size, the higher the contact resistance. This makes contact resistance a significant and sometimes dominant factor in very large scale integration (VLSI) metal system performance. Therefore an important element in the manufacturing and subsequent operation of integrated circuit devices is the electrical contacts and associated contact resistance which are required to conduct the power and signals throughout the integrated circuitry.

For example, for a typical metal oxide semiconductor field effect transistor (MOSFET), these contacts are fabricated through the standard lithographic process utilizing photoresist with optical masks to pattern the contact areas. As illustrated in FIG. 1, a cross section of two typical FET devices are shown. A thin silicon dioxide layer ( $\text{SiO}_2$ ) 12 typically between 80 and 150 Å thick is placed on a substrate 10 as a gate oxide dielectric. This is normally followed by a deposition of polysilicon 14A to a nominal thickness of 3150 Å for the gate control voltage electrode, followed by a tetraethyl orthosilicate (TEOS) oxide layer 16A nominally 3000 Å thick for gate insulation and spacer isolation. After patterning and a TEOS and poly etching processes, a thin layer of silicon nitride (SiN) 22 is deposited to a nominal thickness of 300 Å over the TEOS layer 16A followed by a final contact passivation dielectric of boron phosphorous silicon glass (BPSG) 24 to a nominal thickness of 3000 Å. The structure is subsequently patterned with photoresist (PR) 26 and the contact hole 30A is opened with a wet isotropic etch to produce the structure shape depicted in FIG. 1 in preparation for contact metallization. This contact hole requires a cleaning process that assures good metal contact and subsequent low contact resistance. The final contact opening process is typically a dry etch cleaning step using a gas containing fluorine. This etch is typically followed by a nominal 2 minute buffered oxide etch (BOE) wet dip cleaning step prior to contact metal sputtering. As contact hole dimension is reduced from 2 μm to 1 μm, this BOE premetal dip does not always remove a fluoride residue left from the dry etch process. Since fluorine acts as a donor element, this residue can affect the contact resistance for a P+ to metal contact. This perturbation in contact resistance can effect device performance and impact process yields for small contact hole devices. It is desired to define a method for improving contact cleaning prior to metal deposition thereby improving the metal contact ohmic resistance maintaining or improving device performance and process yields. U.S. Pat. No. 4,752,505 to Arac teaches a pre-metal deposition clean for B—Si—O insulating layer. U.S. Pat. No. 5,486,266 to Tsia et al shows a method of cleaning a silicon contact surface using  $\text{H}_2\text{O}_2$ . U.S. Pat. No. 5,229,334 to Kato shows a method of forming a gate insulating layer by cleaning using  $\text{H}_2\text{O}_2$ . U.S. Pat. No. 5,308,400 to Chen shows a wafer

2

cleaning process using  $\text{H}_2\text{O}_2$ . U.S. Pat. No. 5,670,019 to Huang shows a  $\text{H}_2\text{O}_2$  cleaning process for removing precipitates after a tungsten etchback process. U.S. Pat. No. 5,801,096 to Lee et al shows a method of forming contact holes and filling the holes with metal.

## SUMMARY OF THE INVENTION

Accordingly, it is the primary objective of the invention to provide an effective and manufacturable method for cleaning the surface of a partially manufactured integrated circuit so that a subsequently deposited metal film will adhere well to the surface and have a well controlled contact resistance, thereby enhancing device yield and performance.

Furthermore, it is the objective of the invention to maintain or improve contact resistance while maintaining important device characteristics such as effective channel length ( $L_{eff}$ ) and device threshold voltage ( $V_{tp}$ ).

Yet another object of the invention is to reduce or maintain the contact resistance and the range thereof, as the contact hole dimensions are reduced below 2.0 μm to a nominal 1.0 μm size range.

Another objective of the invention is to simplify the process by eliminating an insulating or passivation layer, while maintaining appropriate insulating, isolation and dielectric properties.

A separate aspect of this invention is to improve gate polysilicon passivation by using a single layer of 5K Å TEOS, or alternatively, using a single layer of 5 to 6K Å BPSG.

The above objectives are achieved by the methods of the invention which describes a process for developing a semiconductor device low resistance electrical contact. In this process a gate oxide layer followed by a polysilicon layer is deposited on the semiconductor substrate in proximity to the device contact area. It is subsequently patterned with photoresist and etched to produce the desired gate structure. This is followed by a deposited layer of silicon dioxide or silicon nitride (SiN) which is appropriately patterned and etched to form gate isolation spacers. Then a nominal 300 Å layer of silicon nitride (SiN) is deposited followed by a layer of tetraethyl orthosilicate (TEOS) or borophosphosilicate glass (BPSG). The contact area is defined by photolithography, and the passivation layers are etched either by a dry etch such as a RIE process, or a combination of a wet BOE process followed by a dry etch, to form the metal contact holes. Prior to sputtering the contact metal, the contact area is cleaned with a dip in a BEO solution, followed by a key aspect of the invention process, a Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ) dip. This  $\text{H}_2\text{O}_2$  cleaning step enables lower device contact resistance for the P+ contact areas which is essential to good device performance. It has the additional benefit of maintaining or enhancing product yield as the contact hole size is decreased to meet the requirements of ever larger scale device integration.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a cross section through 2 adjacent typical field effect transistors showing a prior art structure for making a FET semiconductor device with a 2 μm device contact using a combination of TEOS and BPSG insulation and isolation.

FIG. 2 shows one form of the invention showing a cross section through 2 adjacent typical field effect transistors with a 1 μm contact hole and which utilizes a nominal 3K Å layer of TEOS passivation for the oxide and nominal 3500 Å polysilicon self aligned gate (SAG) structure.

FIG. 3 shows an alternative form of the invention structure by representing a cross section through 2 adjacent

typical field effect transistors for a 1  $\mu\text{m}$  device contact, using a nominal 3500  $\text{\AA}$  polysilicon gate element covered by a layer of silicon nitride ( $\text{SiN}_4$ ) followed by a single layer of either TEOS or BPSG.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to FIG. 2 there is shown a cross section through two adjacent field effect transistors (FET) such as could be part of an integrated circuit. The substrate 10 on which the FET's were built is a body of N type silicon of single crystal orientation. A thin layer of oxide 12 is deposited on the substrate to form the gate oxide whose thickness determines the threshold voltage for the devices. The gate oxide film thickness is normally between 80 and 150  $\text{\AA}$  in thickness and is normally thermally grown by the dry oxidation method using oxygen and hydrogen gases. A layer of polycrystalline silicon (poly) 14B is deposited over the gate oxide, typically by low pressure chemical vapor deposition (LPCVD) to a nominal thickness of 3500  $\text{\AA}$  to serve as the gate electrode of the devices. The poly layer is usually doped with phosphorus or arsenic to increase the conductivity of the electrode. This nominal poly thickness is increased over the prior art shown in FIG. 1 to improve the poly masking ability used in the self aligned gate (SAG) process to shield the FET channel from unwanted dopant contamination during the source/drain heavy doping implant process. This increased poly thickness provides better gate threshold voltage ( $V_{\text{tp}}$ ), control and stability. After appropriate patterning and etching to form the gate structure of oxide 12 and poly 14B, an oxide layer is deposited over the surface and etched to form the gate side spacers 28 to insulate the gate from the source drain.

The source/drain regions are made up of the P+ heavily doped regions 18 and P- lightly doped (LDD) regions 20. These source/drain regions are generally created by means of ion implantation as is well understood in the art. They will be contacted by a metal conductor not shown in the cross section, typically an alloy of aluminum with 2% silicon or a tungsten metallurgy system. The gates are covered by an insulating layer of silicon nitride (SIN) 22 typically deposited by low pressure chemical vapor deposition (LPCVD) or plasma enhanced chemical vapor deposition (PECVD) utilizing silane ( $\text{SiH}_4$ ) or dichlorosilane ( $\text{SiCl}_2\text{H}_2$ ) as source gases to a thickness between 200 and 400  $\text{\AA}$ , with a nominal thickness of 300  $\text{\AA}$ . A layer of TEOS oxide 16B is deposited over the SIN to a thickness typically between 2500 and 3500  $\text{\AA}$  using a PECVD with tetraethyl orthosilicate ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ) source or silane with nitrous oxide in an argon plasma process. A unique feature of this embodiment of the invention places the SIN 22 directly over the poly electrode 14B and side spacer 28 and then uses the nominal 3000  $\text{\AA}$  TEOS 16B in place of the nominal 3000  $\text{\AA}$  BPSG 24 shown in prior art FIG. 1 as the final contact dielectric layer. This saves one masking and deposition step over the prior art.

The SIN 22 and TEOS 16B are subsequently patterned by photoresist 26 and anisotropically etched, typically by a plasma etch or a reactive ion etch (RIE) using fluorine as an etchant to open a contact hole 30B to allow contact to the source/drain and gate areas by a deposited layer of metal. The gate element contact area is not shown in this cross section. The anisotropic etch provides vertical walls of TEOS 16B surrounding the contact hole 30B and eliminating the thinner coverage over the poly step edge caused by the curved surface of the TEOS 16A and SIN 22 isotropic etch shown in FIG. 1.

Just prior to the deposition of the contact metallurgy it is necessary to properly prepare the surface of the device. If this is not done residues may cause a layer of relatively high electrical resistivity between the source/drain diffusion 18

and the metal. Because the area of the contact hole is very small, the absolute value of the resulting contact resistance can be significant and may be greater than what has been specified to be the maximum contact resistance. Therefore, following the etch process, the contact hole is cleaned first by a 30 second dip in a moderate BOE solution typically a ratio of 10 to 1 ammonium fluoride ( $\text{NH}_4\text{F}$ ) hydrofluoric acid (HF) mixed in water, followed by a key aspect of the invention, a dip in an active solution of 49%  $\text{H}_2\text{O}_2$  and water for between 10 and 30 minutes. This  $\text{H}_2\text{O}_2$  cleaning step has the advantage over the previous process of more completely removing the fluoride residues left from the previous dry etch process improving the device contact resistance, and subsequently performance as well as improving product yield. The cleaning process is completed with a deionized water rinse.

FIG. 3 is an alternate embodiment of the invention. For increased passivation protection the nominal 3K  $\text{\AA}$  TEOS layer 16B shown in FIG. 2 can be increased to a nominal 5K  $\text{\AA}$  TEOS 16C thickness shown in FIG. 3. The etching process for this thickness TEOS is first an isotropic wet etch using a BOE solution typically a ratio of 10 to 1 ammonium fluoride ( $\text{NH}_4\text{F}$ ) hydrofluoric acid (HF) mixed in water, for approximately the first 1500  $\text{\AA}$  followed by an anisotropic dry etch such as a RIE process for the nominally 3500  $\text{\AA}$  thick remaining TEOS layer 16C. This process produces the contact hole profile 30C shown in FIG. 3. After the etching process is complete, the contact hole is cleaned using the previously described BOE for a nominal 30 seconds followed by the  $\text{H}_2\text{O}_2$  dip for between 10 and 30 minutes followed by the deionized water rinse. This device passivation profile provides a more robust passivation of the semiconductor devices.

A third embodiment of the invention would be to change the TEOS passivation layer 16C to a BPSG layer with a 6K  $\text{\AA}$  nominal thickness. The etching process for this material would be the same as for the second embodiment, that is, a wet isotropic etch followed by a dry anisotropic etch to provide a similar profile for the contact hole 30C as represented in FIG. 3. After the etching process is complete, the contact hole is cleaned using the previously described BOE for a nominal 30 seconds followed by the  $\text{H}_2\text{O}_2$  dip for between 10 and 30 minutes followed by the deionized water rinse. This device passivation profile also provides a more robust passivation of the semiconductor devices than the prior art process.

It should be understood that while the application of the invention has been described through means of an example based on an FET device contained within an integrated circuit, the scope of the device is not limited to FET's or even integrated circuits.

While the invention has been particularly shown and described with reference to the preferred embodiments thereof, it will be understood by those skilled in the art that various changes in form and details may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. A method of cleaning the surface of a partially manufactured integrated circuit prior to contact metal deposition on said surface comprising:

dipping the said surface in a buffered oxide etch (BOE); then immersing said surface in a solution consisting of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and water; rinsing in deionized water in preparation for metal sputtering.

2. The method of claim 1 where the BOE contains from 8 to 10 parts ammonium fluoride ( $\text{NH}_4\text{F}$ ) to 1 part hydrofluoric acid (HF) mixed water.

3. The method of claim 1 where said BOE dip is for a duration of between 20 and 40 seconds.

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4. The method of claim 1 whereby said hydrogen peroxide bath is composed by volume of between 48% and 50% active parts hydrogen peroxide ( $H_2O_2$ ) to water.

5. The method of claim 1 whereby the duration of said  $H_2O_2$  dip is between 10 and 30 minutes.

6. The method of claim 1 where the resistance of said deionized water is between 16 and 22 megohm-cm.

7. A method of simplifying the process of FET SAG gate passivation of a semiconductor device with a 1 um contact hole on a semiconductor substrate comprising:

depositing a layer of gate oxide on said substrate;  
depositing a doped layer of polysilicon over said gate oxide;

anisotropically etching said poly and gate oxide to form the gate electrode element;

depositing a layer of oxide over said gate electrode element;

isotropically etching said oxide to form gate oxide spacers;

depositing a layer of SIN over said gate structure;

depositing a layer of TEOS over said SIN and said gate structure;

patterning said TEOS and SIN with photoresist to define contact metallization hole;

etching said TEOS and SIN to open said contact hole;

cleaning said contact hole opening with a BOE solution followed by a solution consisting of  $H_2O_2$  and water followed by a deionized water rinse.

8. The method of claim 7 whereby said poly is deposited to a thickness of between about 3400 Å and 3600 Å.

9. The method of claim 7 whereby said SIN passivation is deposited to a thickness of between about 250 Å and 350 Å.

10. The method of claim 7 whereby said TEOS passivation is deposited by CVD processing using tetraethyl orthosilicate as a source to a thickness of between about 2900 Å and 3100 Å.

11. The method of claim 7 wherein said contact hole is created using anisotropic, RIE processing using a fluorine based etchant.

12. The method of claim 7 where said BOE cleaning solution contains from 8 to 10 parts ammonium fluoride ( $NH_4F$ ) to 1 part hydrofluoric acid (HF) mixed with water, and is for a duration of between 20 and 40 seconds.

13. The method of claim 7 whereby said hydrogen peroxide cleaning bath is composed by volume of between 48% and 50% active parts hydrogen peroxide ( $H_2O_2$ ) to water and is between 10 and 30 minutes in duration.

14. The method of claim 7 where the resistance of said deionized water is between 16 and 22 megohm-cm.

15. A method of improving FET SAG gate passivation of a semiconductor device with a 1 um contact hole on a semiconductor substrate comprising:

depositing a layer of gate oxide on said substrate;

depositing a doped layer of polysilicon over said gate oxide;

anisotropically etching said poly and gate oxide to form the gate electrode element;

depositing a layer of oxide over said gate electrode element;

isotropically etching said oxide to form gate oxide spacers;

depositing a layer of SIN over said gate structure;

depositing a layer of TEOS over said SIN and said gate structure;

patterning said TEOS and SIN with photoresist to define contact metallization hole;

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performing an isotropic partial etch on said TEOS;  
completing said etch using an anisotropic etch on remaining said TEOS and said SIN;

cleaning said contact hole opening with a BOE solution followed by a solution consisting of  $H_2O_2$  and water followed by a deionized water rinse.

16. The method of claim 15 whereby said poly is deposited to a thickness of between about 3400 Å and 3600 Å.

17. The method of claim 15 whereby said SIN passivation is deposited to a thickness of between about 250 Å and 350 Å.

18. The method of claim 15 whereby said TEOS passivation is deposited by CVD processing using tetraethyl orthosilicate as a source to a thickness of between about 4800 Å and 5200 Å.

19. The method of claim 15 wherein said contact hole is created using an isotropic wet etch to remove between 1300 Å and 1700 Å of the TEOS.

20. The method of claim 15 wherein an anisotropic dry etch of said TEOS and said SIN is performed to open said contact hole to said source/drain substrate surface.

21. The method of claim 15 where said BOE cleaning solution contains from 8 to 10 parts ammonium fluoride ( $NH_4F$ ) to 1 part hydrofluoric acid (HF) mixed with water, and is for a duration of between 20 and 40 seconds.

22. The method of claim 15 whereby said hydrogen peroxide cleaning bath is composed by volume of between 48% and 50% active parts hydrogen peroxide ( $H_2O_2$ ) to water and is between 10 and 30 minutes in duration.

23. The method of claim 15 where the resistance of said deionized water is between 16 and 22 megohm-cm.

24. A method of improving FET SAG gate passivation of a semiconductor device with a 1 um contact hole on a semiconductor substrate comprising:

depositing a layer of gate oxide on said substrate;

depositing a doped layer of polysilicon over said gate oxide;

anisotropically etching said poly and gate oxide to form the gate electrode element;

depositing a layer of oxide over said gate electrode element;

isotropically etching said oxide to form gate oxide spacers;

depositing a layer of SIN over said gate structure;

depositing a layer of BPSG over said SIN and said gate structure;

patterning said BPSG and SIN with photoresist to define contact metallization hole;

etching said BPSG and SIN to open said contact hole;

cleaning said contact hole opening with a BOE solution followed by a solution consisting of  $H_2O_2$  and water followed by a deionized water rinse.

25. The method of claim 24 whereby said poly is deposited to a thickness of between about 3400 Å and 3600 Å.

26. The method of claim 24 whereby said SIN passivation is deposited to a thickness of between about 250 Å and 350 Å.

27. The method of claim 24 whereby said BPSG passivation is deposited by CVD processing using tetraethyl orthosilicate as a source to a thickness of between about 5800 Å and 6200 Å.

28. The method of claim 24 wherein said contact hole is created using an isotropic wet etch to remove between 1300 Å and 1700 Å of the TEOS.

29. The method of claim 24 wherein an anisotropic dry etch of said TEOS and said SIN is performed to open said contact hole to said source/drain substrate surface.

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30. The method of claim 24 where said BOE cleaning solution contains from 8 to 10 parts ammonium fluoride ( $\text{NH}_4\text{F}$ ) to 1 part hydrofluoric acid ( $\text{HF}$ ) mixed with water, and is for a duration of between 20 and 40 seconds.

31. The method of claim 24 whereby said hydrogen peroxide cleaning bath is composed by volume of between

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48% and 50% active parts hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to water and is between 10 and 30 minutes in duration.

32. The method of claim 24 where the resistance of said deionized water is between 16 and 22 megohm-cm.

\* \* \* \* \*



US005868150A

**United States Patent** [19][11] **Patent Number:** **5,868,150****Mohindra et al.**[45] **Date of Patent:** **Feb. 9, 1999**[54] **ULTRA-LOW PARTICLE SEMICONDUCTOR CLEANER**[75] Inventors: **Raj Mohindra**, Los Altos; **Abhay Bhushan**, Palo Alto; **Rajiv Bhushan**, Mountain View; **Suraj Puri**, Los Altos; **John H. Anderson, Sr.**, Milpitas; **Jeffrey Nowell**, San Francisco, all of Calif.

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[22] Filed: **May 22, 1997**

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**Related U.S. Application Data**

[60] Division of Ser. No. 555,634, Nov. 8, 1995, Pat. No. 5,772,784, which is a continuation-in-part of Ser. No. 437,541, May 9, 1995, Pat. No. 5,571,337, which is a continuation-in-part of Ser. No. 339,326, Nov. 14, 1994, Pat. No. 5,634,978.

[51] Int. Cl.<sup>6</sup> ..... **B08B 3/04**[52] U.S. Cl. .... **134/135; 134/201; 134/902; 134/186; 211/48.18**[58] Field of Search ..... **134/135, 201, 134/902, 25.4, 25.5, 30, 155, 186; 211/48.18; 206/832**

(List continued on next page.)

**Primary Examiner**—Frankie L. Stinson**Attorney, Agent, or Firm**—Townsend and Townsend and Crew LLP

[57]

**ABSTRACT**

A method (400) for cleaning a semiconductor wafer. The method includes immersing (420) a wafer in a liquid comprising water. The wafer has a front face, a back face, and an edge. The method also includes providing a substantially particle free environment adjacent to the front face and the back face as the liquid is being removed. A step of introducing a carrier gas comprising a cleaning enhancement substance during the providing step (450) also is included. The cleaning enhancement substance dopes the liquid which is attached to the front face and the back face to cause a concentration gradient of the cleaning enhancement substance in the attached liquid to accelerate fluid flow of the attached liquid off of the wafer.

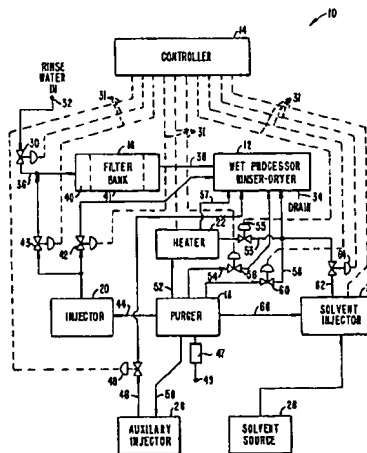
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**37 Claims, 9 Drawing Sheets**

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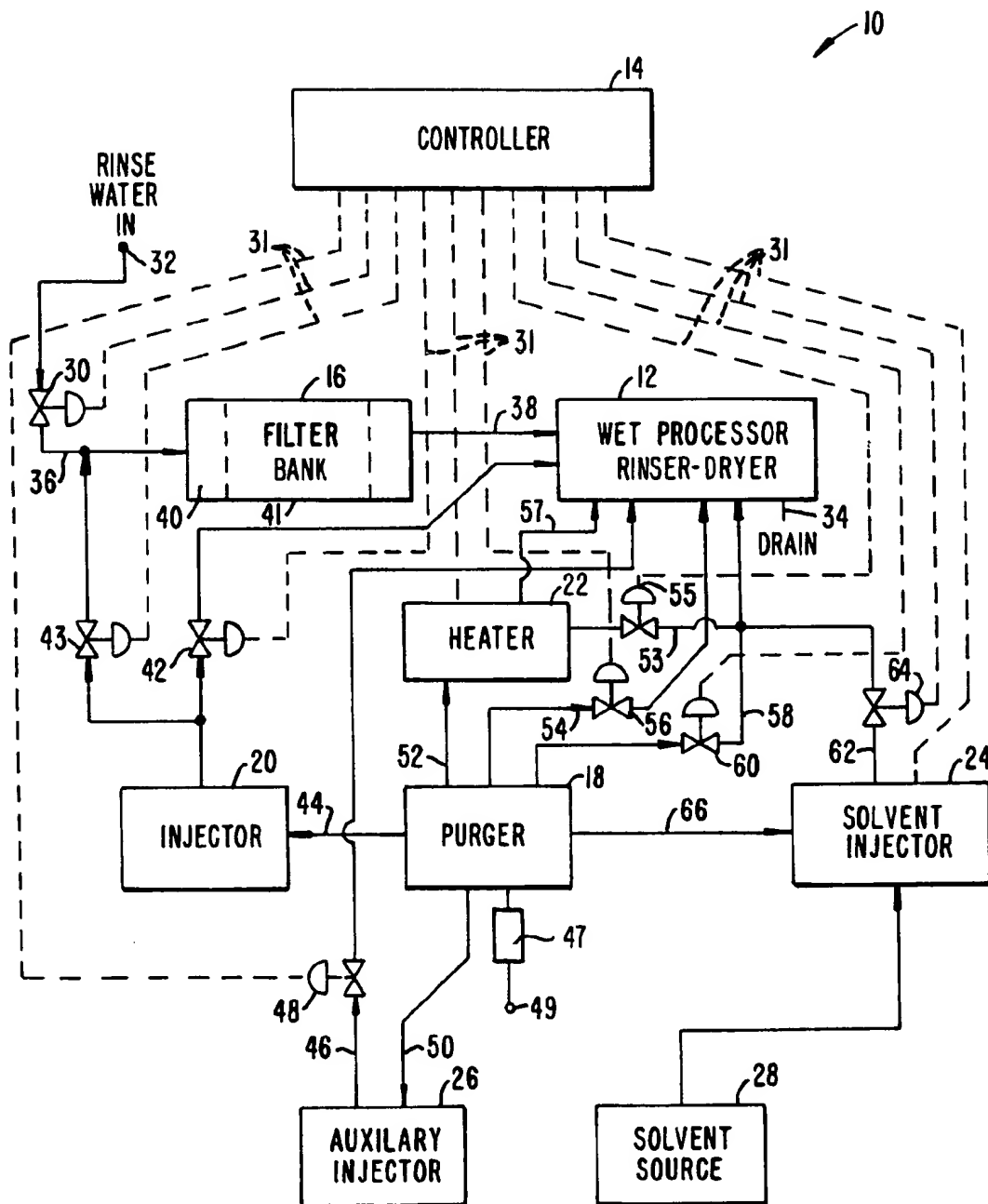
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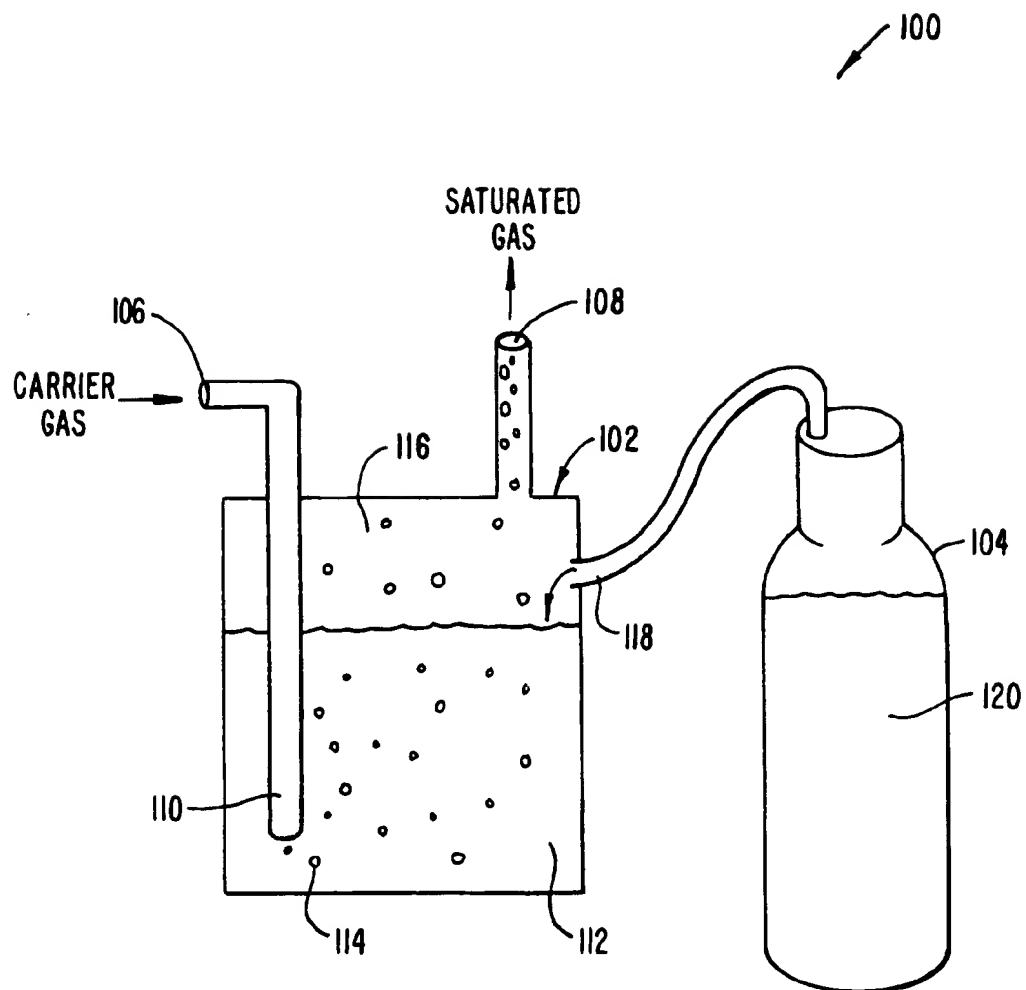
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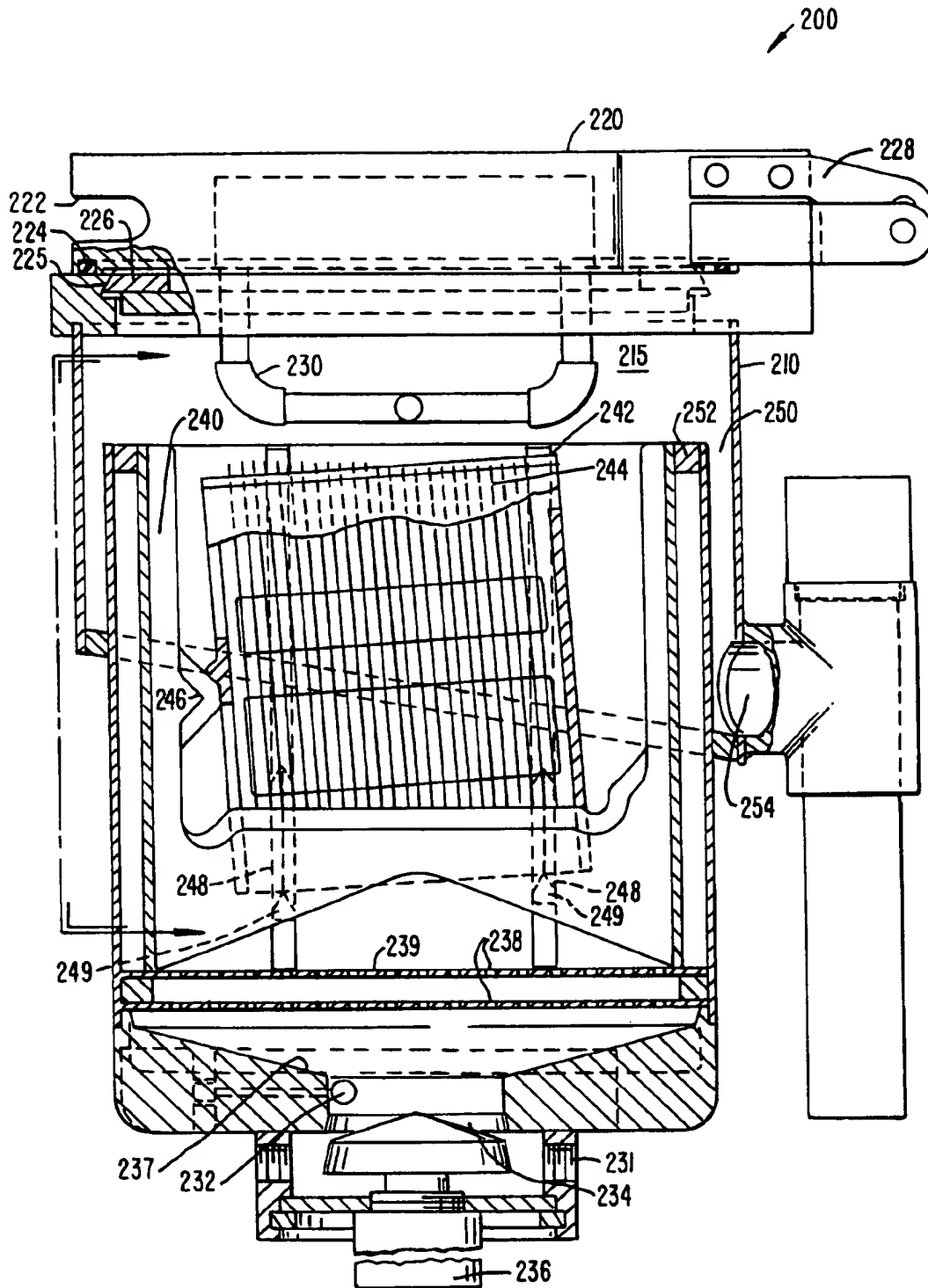
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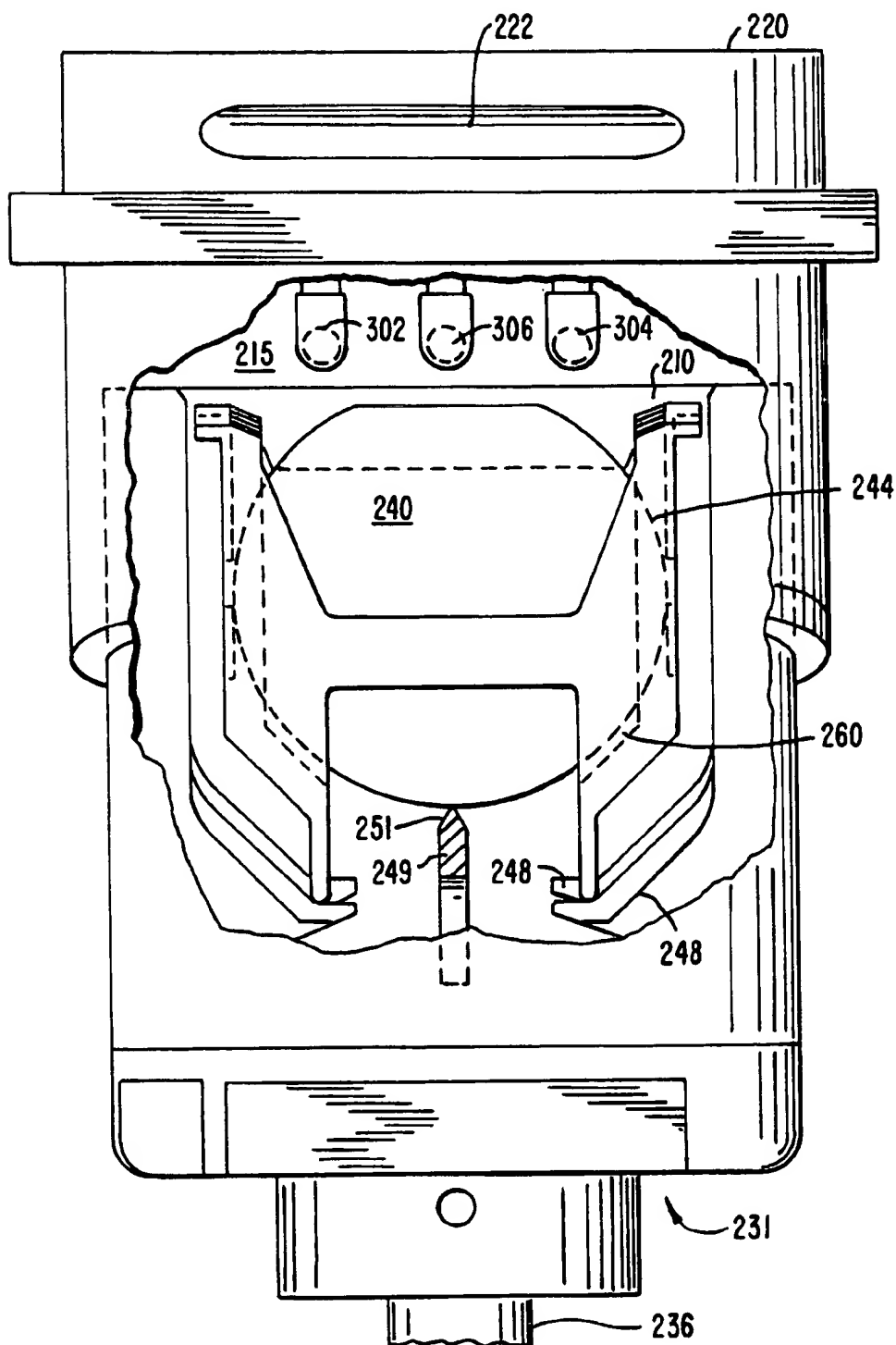
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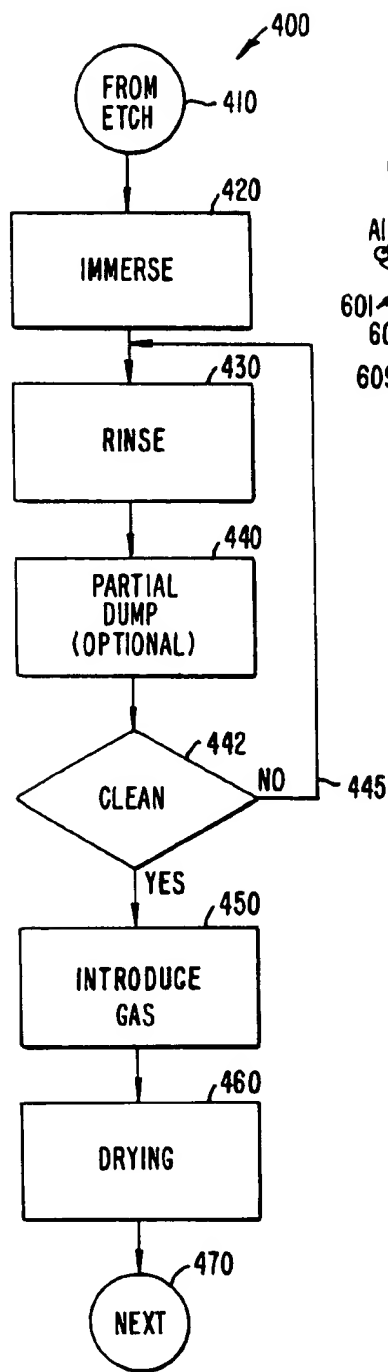
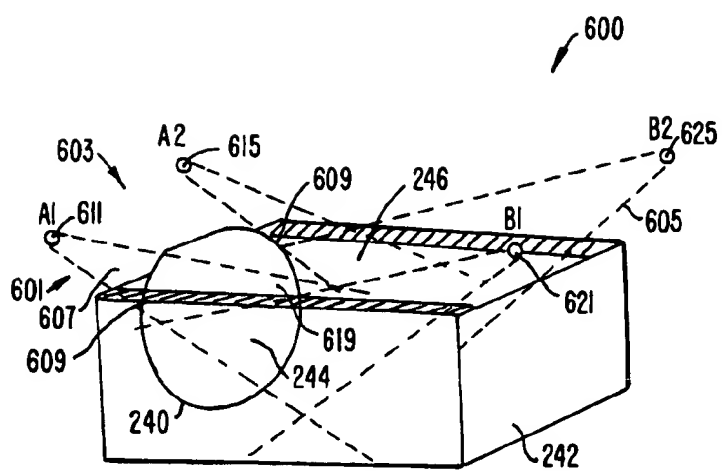
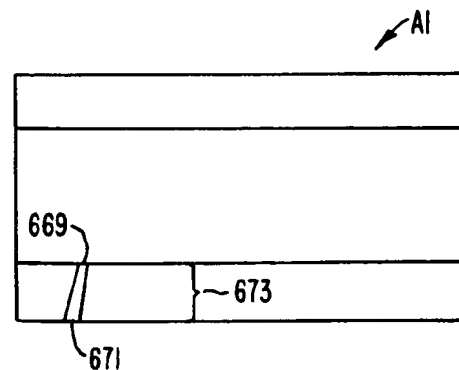
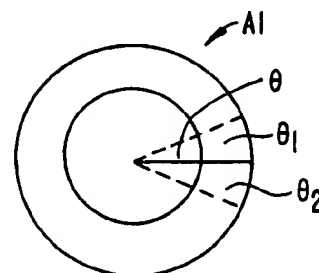
**FIG. 1.**

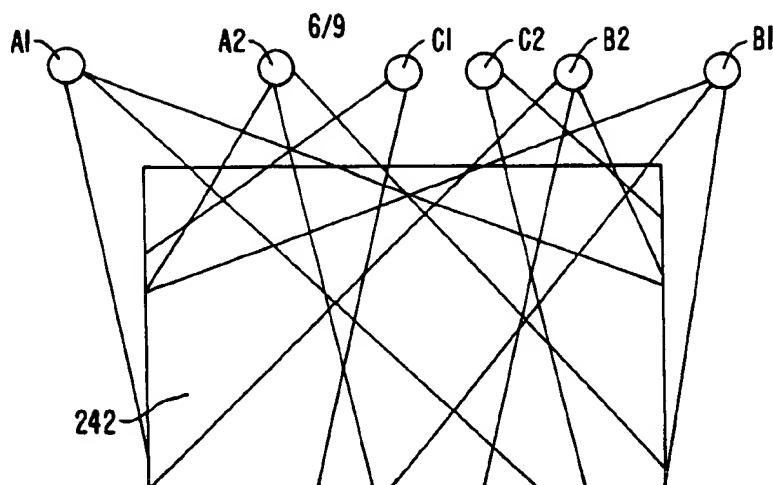
**FIG. 2.**

**FIG. 3.**

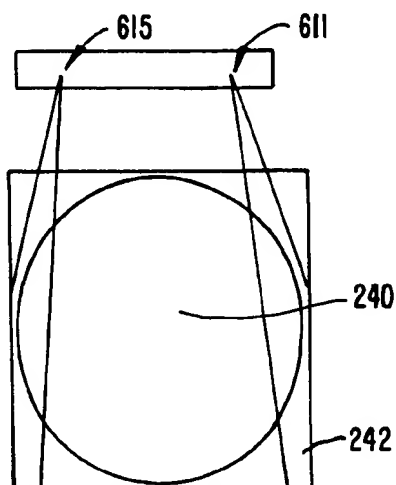


**FIG. 4.**

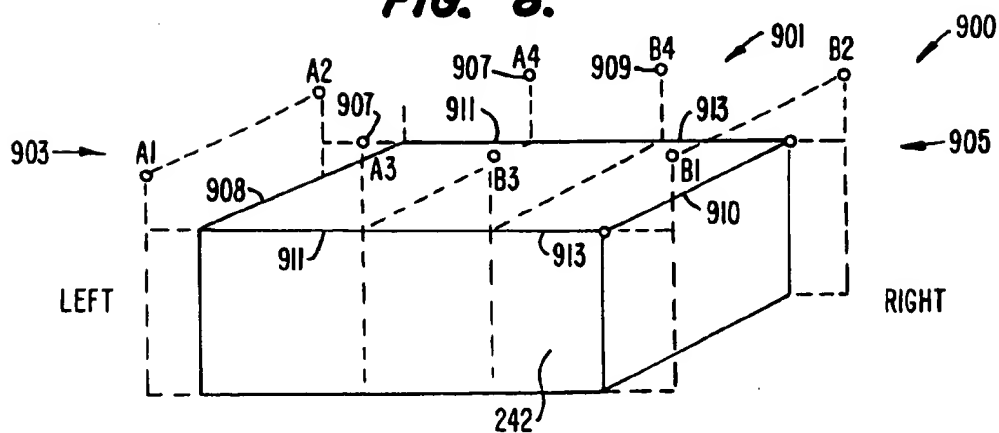
**FIG. 5.****FIG. 6.****FIG. 6A.****FIG. 6B.**



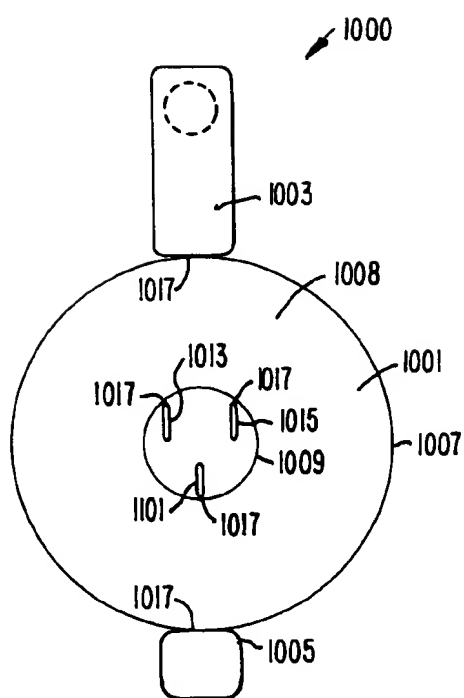
**FIG. 7.**



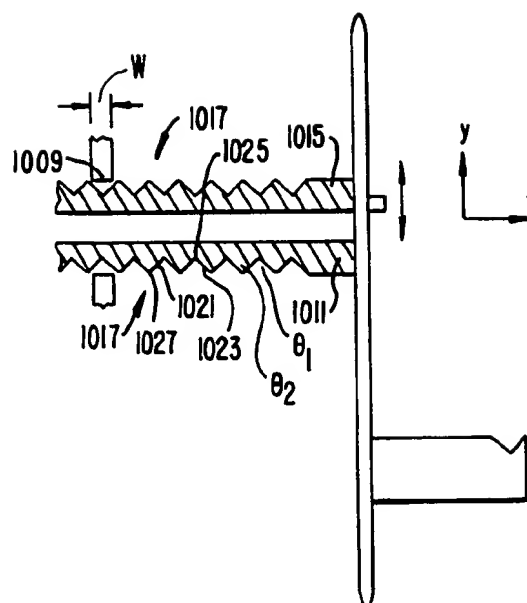
**FIG. 8.**



**FIG. 9.**

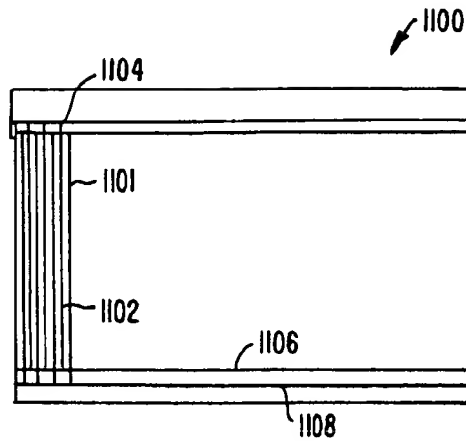


**FIG. 10A.**

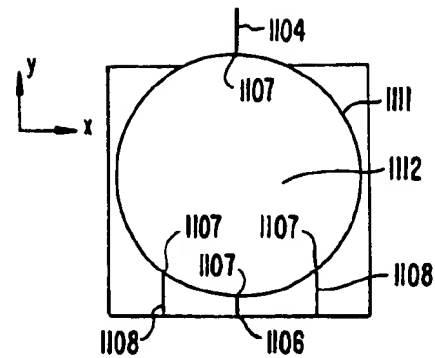


**FIG. 10B.**

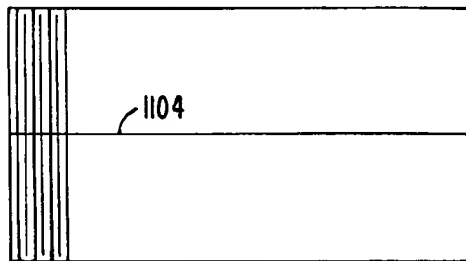




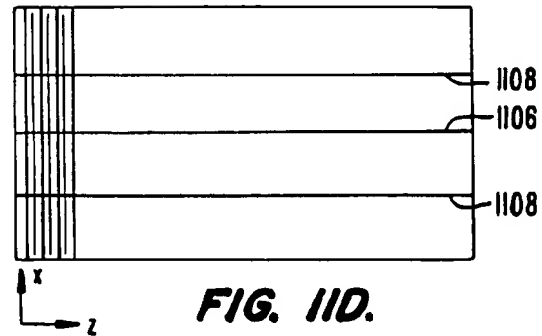
**FIG. 11A.**



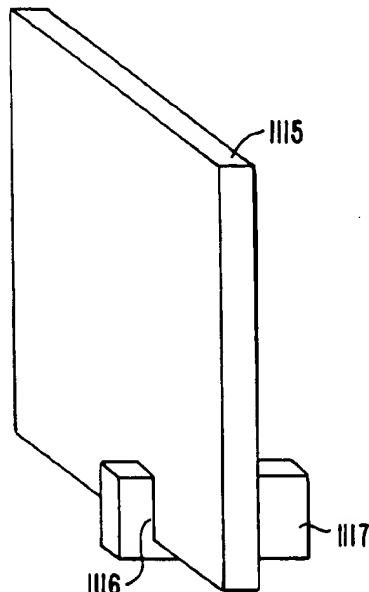
**FIG. 11B.**



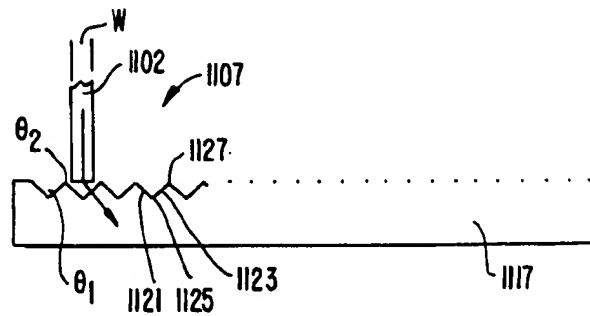
**FIG. 11C.**



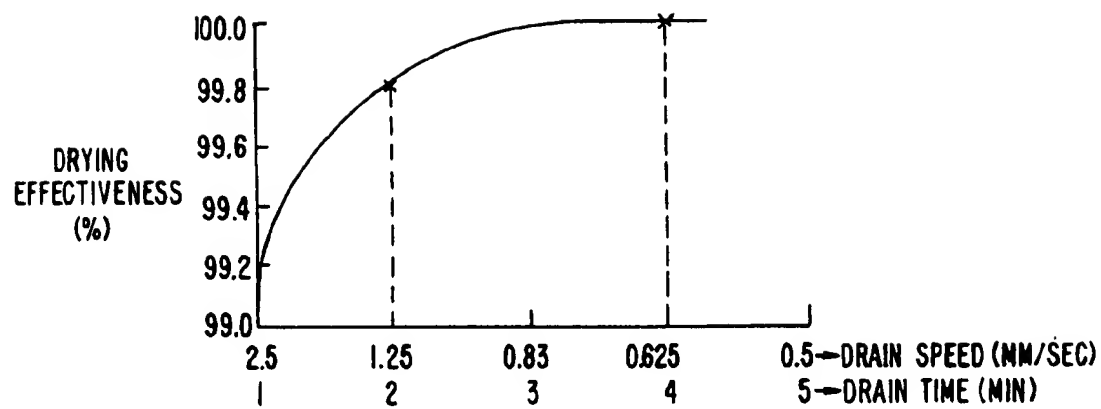
**FIG. 11D.**



**FIG. 11E.**



**FIG. 11F.**

**FIG. 12.**

# ULTRA-LOW PARTICLE SEMICONDUCTOR CLEANER

## CROSS-REFERENCE TO RELATED APPLICATIONS

This is a division of application Ser. No. 08/555,634, filed Nov. 8, 1995 now U.S. Pat. No. 5,772,784, which is a continuation-in-part of application Ser. No. 08/437,541, filed May 9, 1995 now U.S. Pat. No. 5,571,337, which is a continuation-in-part of application Ser. No. 08/339,326, filed Nov. 14, 1994 now U.S. Pat. No. 5,634,978, the disclosure of which is incorporated by reference.

## BACKGROUND OF THE INVENTION

The present invention relates to the field of semiconductor integrated circuits. The invention is illustrated in an example with regard to a semiconductor integrated circuit cleaning technique, including a method and apparatus, but it will be recognized that the invention has a wider range of applicability. Merely by way of example, the invention can also be applied to the manufacture of raw wafers, lead frames, medical devices, disks and heads, flat panel displays, micro-electronic masks, and other applications requiring high purity wet processing such as steps of rinsing, cleaning, drying, and the like.

Industry utilizes or has proposed various techniques to rinse and dry a semiconductor wafer. An example of a conventional technique used to rinse a wafer is a cascade rinse. The cascade rinse utilizes a cascade rinser which includes inner and outer chambers, each separated by a partition. Rinse water flows from a water source into the inner chamber. The rinse water from the inner chamber cascades into the outer chamber. An in-process wafer such as an etched wafer is typically rinsed in the cascade rinser by dipping the etched wafer into the rinse water of the inner chamber. This process is often used to neutralize and remove acid from the etched wafer.

A limitation with the cascade rinser is that "dirty water" often exists in the first chamber. The dirty water typically includes residual acid as well as "particles" which often attach to the wafer. These particles often cause defects in the integrated circuit, thereby reducing the number of good dies on a typical wafer. Another limitation with the cascade rinser is wafers from the cascade rinser must still undergo a drying operation. A subsequent drying operation often introduces more particles onto the integrated circuit. More particles on the integrated circuit typically further decrease the number of good dies on the wafer. Accordingly, the cascade rinse often cannot clean or remove particles from the wafer.

Another technique often used to rinse wafers is the "quick dump" method. The quick dump method relies upon the rapid deployment of water from the rinse tank to remove water and impurities from the semiconductor wafer. A limitation with this method is its inability to actually clean or remove particles from the wafer. In fact, the rapid deployment of water from the tank often transfers more particles onto the wafer. In addition, the wafers from the quick dump tank must still undergo a drying operation, further increasing the number of particles on the wafer. As previously noted, more particles often relates to lower die yields on the semiconductor wafer.

A further technique used to both rinse and dry wafers relies upon a spin rinse/dryer. The spin rinse/dryer uses a combination of rinse water spray to rinse and centrifugal force to remove water from the semiconductor wafer. The dry step often removes the water from the semiconductor

wafer substantially by centrifugal force and evaporation. However, the spin rinse/dryer often introduces more particles onto the wafer. In fact, initially dissolved or suspended contaminants such as particles in the water are often left on the semiconductor wafer, thereby reducing the number of good dies on the wafer. Another limitation with the spin rinse/dryer is its complex mechanical design with moving parts and the like. The complex mechanical design often leads to certain problems such as greater downtime, wafer breakage, more spare parts, greater costs, among others. A further limitation is static electricity often builds up on the wafers during the spin cycle, thereby attracting even more particles onto the surface of the semiconductor. Accordingly, the spin rinse/drying does not clean or remove particles from the wafer.

Other techniques used to dry wafers include an isopropyl alcohol (IPA) vapor dryer, full displacement IPA dryer, and others. These IPA-type dryers often rely upon a large quantity of a solvent such as isopropyl alcohol and other volatile organic liquids to facilitate drying of the semiconductor wafer. An example of such a technique is described in U.S. Pat. No. 4,911,761, and its related applications, in the name of McConnell et al. and assigned to CFM Technologies, Inc. McConnell et al. generally describes the use of a superheated or saturated drying vapor as a drying fluid. This superheated or saturated drying vapor often requires the use of large quantities of a hot volatile organic material. The superheated or saturated drying vapor forms a thick organic vapor layer overlying the rinse water to displace (e.g., plug flow) such rinse water with the drying vapor. The thick organic vapor layer forms an azeotropic mixture with water, which will condense on wafer surfaces, and will then evaporate to dry the wafer.

A limitation with this type of dryer is its use of the large solvent quantity, which is hot, highly flammable, and extremely hazardous to health and the environment. Another limitation with such a dryer is its cost, which is often quite expensive. In fact, this dryer needs a vaporizer and condenser to handle the large quantities of hot volatile organic material. Still further, it has been determined that large quantities of hot volatile organic material are typically incompatible with most photoresist patterned wafers, and are also detrimental to certain device structures.

Still another technique relies upon a hot deionized (DI) process water to rinse and promote drying of the semiconductor wafer. By way of the hot DI water, the liquid on the wafer evaporates faster and more efficiently than standard room temperature DI water. However, hot water often produces stains on the wafer, and also promotes build-up of bacterial and other particles. Hot water can also damage the semiconductor, thereby reducing the amount of good dies on the wafer. Another limitation is water is often expensive to heat, and hot DI water is also an aggressive solvent. As an aggressive solvent, it often deteriorates equipment and facilities, thereby increasing maintenance operation costs.

As line size becomes smaller and the complexity of semiconductor integrated circuits increases, it is clearly desirable to have a cleaning technique, including a method and apparatus, that actually removes particles, prevents additional particles, and does not introduce stains on the wafers. The cleaning technique should also dry the wafers, without other adverse results. A further desirable characteristic includes reducing or possibly eliminating the residual water left on wafer surfaces and edges when water is removed (a meniscus). The water left on such surfaces and edges often attracts and introduces more particles onto the semiconductor wafer. The aforementioned conventional

techniques fail to provide such desired features, thereby reducing the die yield on the semiconductor during wet processes.

From the above, it is seen that a cleaning method and apparatus for semiconductor integrated circuits that is safe, easy, and reliable is often desired.

#### SUMMARY OF THE INVENTION

The present invention provides a safe, efficient, and economical method and apparatus to clean an article (or object) such as a semiconductor wafer. In particular, the present method provides an improved technique that actually removes or reduces the amount of particles from the semiconductor substrate and also effectively cleans the substrate. The present method also provides an in situ cleaning system with substantially no mechanical movement of the substrate.

One aspect of the present invention provides a method for cleaning a semiconductor wafer. The present method includes immersing a wafer in a liquid comprising water. The wafer has a front face, a back face, and an edge. The method also includes providing a substantially particle free environment (e.g., ultra-clean gas, ultra-clean non-reactive gas, etc.) adjacent to the front face and the back face as the liquid is being removed. A step of introducing a carrier gas comprising a cleaning enhancement substance (e.g., trace amount of polar organic compound, helium, surfactants, carbon dioxide, etc.) during the providing step also is included. The cleaning enhancement substance dopes the liquid which is attached to the front face and the back face to cause a concentration gradient of the cleaning enhancement substance in the attached liquid to accelerate fluid flow of the attached liquid off of the wafer.

Another aspect of the invention provides an apparatus for cleaning a semiconductor wafer. The present apparatus includes a vessel adapted to immerse a wafer in a liquid comprising water. This wafer includes a front face, a back face, and an edge. The apparatus also includes a first control valve operably coupled to the vessel, and adapted to provide a substantially particle free environment adjacent to the front face and the back face as the liquid is being removed. A second control valve operably coupled to the vessel also is provided. The second control valve is adapted to introduce a carrier gas comprising a cleaning enhancement substance. The cleaning enhancement substance dopes the liquid which is attached to the front face and the back face to cause a concentration gradient of the cleaning enhancement substance in the attached liquid to accelerate fluid flow of the attached liquid off of the wafer.

A further alternative embodiment provides an apparatus for holding a plurality of substrates. The apparatus includes a lower support. The lower support comprises a plurality of first ridges, where each of the first ridges provides a support for a lower substrate portion. The apparatus also includes an upper support. The upper support comprises a plurality of second ridges, where each of the second ridges provides a support for an upper substrate portion. The lower substrate portion and the upper substrate portion are defined on a substrate. The first ridges and the second ridges draw liquid from the substrate.

A further understanding of the nature and advantages of the present invention may be realized by reference to the latter portions of the specification and attached drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a simplified block diagram of an embodiment of the cleaning system according to the present invention;

FIG. 2 is a simplified cross-sectional view of a solvent bubbler according to the present invention;

FIG. 3 is a simplified cross-sectional side-view of an embodiment of the cleaning chamber;

FIG. 4 is a simplified cross-sectional front-view of an embodiment of the cleaning chamber;

FIG. 5 is a simplified flow diagram of an embodiment of the cleaning method according to the present invention;

FIG. 6 is a simplified diagram of a high velocity flow apparatus according to the present invention;

FIGS. 6A and 6B illustrate simplified diagrams of a nozzle according to the present invention;

FIGS. 7 and 8 are simplified fluid flow diagrams of the high velocity flow apparatus of FIG. 6;

FIG. 9 is a simplified diagram of an alternative embodiment of the high velocity flow apparatus according to the present invention;

FIGS. 10A-10B are simplified cross-sectional view diagrams of an alternative embodiment of a substrate carrier according to the present invention;

FIGS. 11A-11F are simplified cross-sectional view diagrams of an alternative embodiment of a substrate carrier according to the present invention; and

FIG. 12 illustrates drying effectiveness as a function of drain speed for an experiment performed according to the present invention.

#### DESCRIPTION OF THE SPECIFIC EMBODIMENT

FIG. 1 illustrates in block diagram form an embodiment of the cleaning system 10 according to the present invention. The cleaning system 10 includes elements such as a wet processor 12, a controller 14, a filter bank 16, a purger 18, an injector 20, a heater 22, a solvent bubbler 24, an auxiliary injector 26, and a solvent source 28. The system also includes a plurality of flow control valves 30. Each of the flow control valves is operably coupled to the controller 14 and at least one of the aforementioned elements, as shown by dashed lines 31. The solid lines represent lines used to transfer fluids between each of the system elements. A rinse water source 32 and drain 34 are also shown.

Rinse water enters the system at the rinse water source 32. A control valve at the rinse water source 32 controls the flow of rinse water via the controller 14, operably coupled to the control valve 30. The rinse water is a filtered liquid such as deionized (DI) water, among others. Typically the DI water originates from a DI water pad, often outside a wafer fabrication plant.

The filter bank can be any suitable combination of filters, typically used for point of use applications. The filter bank connects to the rinse water source through a line 36 and connects to the wet processor through a line 38. The filter bank includes an ion exchange module 40, a combination of charged and neutral filters 41, among others. This filter bank provides point of use ultra-purified water. The ultra-purified water is substantially free from particles greater than about 0.5 microns, and preferably greater than about 0.2 microns, and more preferably greater than about 0.1 microns.

Examples of charged filters are described and illustrated in Application Ser. No. 08/285,316, filed Aug. 3, 1994, entitled METHOD AND APPARATUS FOR DELIVERING ULTRA-LOW PARTICLE COUNTS IN SEMICONDUCTOR MANUFACTURING (hereinafter "ULTRA-LOW PARTICLE COUNTS") assigned to the present assignee,

and hereby incorporated by reference for all purposes. The filter bank provides for ultra-purified DI water with particles no greater than 0.5 microns in diameter, and preferably 0.2 microns in diameter and less and more preferably 0.1 microns in diameter and less.

The filter bank also provides for a nominal pressure drop therethrough. The pressure drop is less than about 15 pounds per square inch, and preferably less than about 5 pounds per square inch. A higher flow rate is achieved through the filter bank without auxiliary pumps or flow/pressure enhancing devices. Of course, other filters capable of providing ultra-purified water for point of use applications can be used depending upon the application.

The injector 20 can be any suitable injector for reducing or preferably eliminating metal contaminants from lines and system elements. Preferably, the injector 20 is a hydrochloric acid injector. An example of an injector is discussed in ULTRA-LOW PARTICLE COUNTS. The injector connects to the wet processor 12. A control valve 42 meters the acid into the wet processor 12, and a control valve 43 meters the acid into the filter bank 16. Preferably, the controller 14 meters such acid into the system elements such as the wet processor 12 and the filter bank 16, among others during system maintenance, and other desirable times. The injector also connects via line 44 to the purger 18. The purger provides clean pressurized gas to the injector to allow such acid to be introduced into the aforementioned system elements without other auxiliary devices. Of course, the type of injector used depends upon the particular application.

A use of another chemical such as a solvent, hydrogen peroxide, surfactant, cleaning solution, or the like is optionally introduced through the auxiliary injector 26. The auxiliary injector connects to the wet processor through a line 46, and is controlled by a control valve 48 operably coupled to the controller 14. A purger supplying pressurized gas also connects to the auxiliary injector 26 through a line 50. An example of an auxiliary injector and its operation is also illustrated in the ULTRA-LOW PARTICLE COUNTS. Of course, the type of auxiliary injector used depends upon the particular application.

A further system element is the purger 18, often used to supply gas and/or a pressure head to certain system elements such as the wet processor and others. The purger can be any suitable type of pressure reduction and/or control means capable of supplying the source gas to certain system elements at the desired pressure and flow rate. The purger connects to a source gas 49, which is often a carrier gas used in the cleaning system.

Purger 49 also couples to filter 47 before the gas source. This filter 47 is capable of high flow rates, e.g., 1500 standard liters/minute and greater. Filter 47 also has a retention rating at 0.003 microns. Preferably, no less than about 99.999999% of particles are removed by way of filter 47. The filter 47 is coupled between the facilities and cleaning system 10. The filter 47 is located before or immediately before the cleaning system 10. In one embodiment, the filter 47 is attached to the cleaning system, but also can be at other locations. This filter provides for a substantially particle free environment. That is, the gas is substantially free from particles greater than about 0.2 microns, or greater than about 0.1 microns, or greater than about 0.05 microns, or greater than about 0.025 microns, or more preferably greater than about 0.01 microns and less. An example of such a filter is product made by Wafergard T-Line Cartridge Filters. Of course, other filters can be used depending upon the application.

Preferably, the carrier gas is an ultra-purified or electronic grade nitrogen gas, or any suitable carrier gas capable of carrying a cleaning enhancement substance (e.g., a trace of polar organic compound, etc.) into the wet processor at a desired temperature, pressure, and flow rate. The suitable carrier gas also includes a high purity level to prevent contamination of the system elements. An example of a purger is illustrated in ULTRA-LOW PARTICLE COUNTS. The carrier gases (or gas) is also ultra-clean or substantially free from particles greater than about 0.1 microns and preferably greater than about 0.05 microns. As previously noted, the purger also supplies pressurized carrier gas to the bubbler 20 and auxiliary injector 26 through lines 44 and 50, respectively. The purger further supplies gas to the wet processor through certain alternative routes.

A typical route connects the purger 18 to the wet processor 12 through the heater 22 via lines 52 and 57. In this route, the gas can be heated at the heater 22 before entering into the wet processor 12 through the line 57. The heater can be any suitable commercially available or custom made heater capable of heating the gas such as nitrogen to a temperature at the wet processor 12 greater than 70° F. and preferably greater than 150° F., but no greater than 200° F. The controller is operably coupled to the heater to adjust the temperature of the gas and turn-on and turn-off the gas at the desired times. Preferably, however, the gas is at room temperature, and is not heated. The controller also meters the gas into the wet processor at a desired flow rate and time.

Alternatively, the heated gas (a carrier gas) connects to the solvent bubbler 24 through a line 53, before entering the wet processor 12. The heated carrier gas mixes and dilutes solvent from the solvent bubbler 24 before entering the wet processor 12. The controller 14 is operably coupled to a control valve 55 to meter the heated carrier gas to the wet processor 12.

Another alternative route connects the purger 18 directly to the wet processor 12 through a line 54. The controller 14 is operably coupled to a control valve 56 to turn-on and turn-off the gas at the desired times. The controller 14 and the control valve 56 also meter the gas into the wet processor 12 at a desired flow rate and time.

In a further alternative route, the purger 18 connects to the solvent bubbler 24 through a line 58 before entering the wet processor 12. In this route, the carrier gas mixes with solvent (a cleaning enhancement substance) from the solvent bubbler 24 before entering the wet processor 12. The controller is operably coupled to a control valve 60 that meters the carrier gas to the wet processor through the line 58. In one embodiment, the carrier gas contains a trace of polar organic solvent. This carrier gas contains a cleaning enhancement substance which increases fluid flow and cleans off objects to be cleaned. Of course, the use of any of these configurations or combinations of such configurations depends upon the particular application.

The controller 14 can be any suitable microprocessor based programmable logic controller, personal computer controller, or the like for process control. A suitable controller includes features such as programmability, reliability, flexibility, and durability from corrosive elements. The suitable controller includes various input/output ports used to provide connections to open and close valves, regulate and meter fluids, among other features. The controller also includes sufficient memory to store process recipes for desired applications. An example of a suitable controller is illustrated in the ULTRA-LOW PARTICLE COUNTS. Of course, the type of controller used depends upon the particular application.

The solvent bubbler 24 supplies a carrier gas comprising a trace amount of polar organic compound (a cleaning enhancement substance) to the wet processor 12 through line 62. Preferably, the cleaning enhancement substance is a trace of solvent. The purger 18 supplies the carrier gas to the solvent bubbler through line 66. To regulate or meter the flow of the solvent into the wet processor, the controller operably couples a control valve 64 connected to the line 66, attached to the solvent bubbler. The system also provides the solvent source 28 such as a bottle or canister of the desired chemical.

The solvent bubbler can be any suitable solvent bubbler system for use with the wet processor, carrier gas, and solvent. An example of a solvent bubbler system is represented by the simplified illustration of FIG. 2. The solvent bubbler system 100 includes a solvent bubbler vessel 102 and a solvent source 104. The solvent bubbler vessel 102 connects to a carrier gas source at an inlet 106. A sparger 110 sparges carrier gas 114 as bubbles into the solvent 112 at a lower portion of the solvent bubbler vessel. As the carrier gas bubbles float up through the solvent, the carrier gas bubbles accumulate with solvent. Carrier gas bubbles with solvent escape into the vapor head space 116 of the solvent bubbler vessel 102, and exit the solvent bubbler vessel through outlet line 108. This carrier gas with solvent generally behaves according to ideal gas laws or the like. A solvent fill inlet 118 also is connected to the solvent bubbler vessel 102. A solvent source 104 and solvent 120 are further shown. Alternatively, the solvent can be introduced into the carrier gas by mechanical means, e.g., ultrasonic, megasonic, mister, etc.

FIG. 3 is a simplified cross-sectional side-view 200 embodiment of the cleaning chamber according to the present invention. The side-view embodiment 200 includes a main chamber 210, a lid 220, a lower drain region 231, and other elements. The main chamber 210 includes the process region 240 (or lower chamber region) and upper chamber region 215. A cascade drain region 250 also is shown. Of course, other chamber elements also may be present depending upon the particular application.

The lid 220 is preferably a sealed lid. The sealed lid includes a handle 222, O-ring type seal 224, a compression ring 226, a hinge 228, a gas inlet 230, among other features. The compression ring 226 provides outward force onto a horizontal portion 225 of the main chamber housing to seal the contents of the main chamber. The O-ring type seal 224 provides a horizontal seal between vertical surfaces of the lid and main chamber housing. The gas inlet 230 includes at least a carrier gas inlet and solvent gas inlet. Of course, the exact configuration of the gas inlet depends upon the particular application.

The process region 240 includes a substrate carrier 242, substrate carrier support 246, 248, and substrate support 249. As will be described in greater detail below, the substrate carrier and substrate support are configured and arranged to minimize liquid accumulation as liquid is drained away in the drying process.

In a specific embodiment, the substrate carrier is a wafer boat or alternatively a half wafer boat or any other type of substrate carrier with a lower profile. The half wafer boat or lower profile boat holds or accumulates less liquid than its full boat counterpart, and therefore drains liquid faster and more easily. The carrier includes substrates (e.g., wafers) 244 disposed within the supports of the carrier. The carrier is supported by a side substrate carrier support 246 and bottom substrate carrier support 248. The side substrate

carrier support holds the substrate carrier in place, and prevents such substrate carrier from excessive movement. As shown, the bottom substrate support tilts the substrate carrier in a slight angle from a horizontal position. The angle tends to prevent substrates from sticking to each other during certain rinse and dry operations. The angle from the horizontal position ranges from about 2° to about 15°, and is preferably determined by the characteristics of the particular carrier. By keeping each of the substrates separated, liquid does not accumulate therebetween, thereby decreasing the amount of liquid and therefore particles from accumulating on the substrate.

Each substrate carrier support includes a contact point on the substrate carrier to drain liquid such as water from the substrate carrier surface. The contact point is typically a knife edge, serrated edge, or any other shape that breaks the surface tension of the liquid on the substrate carrier surface. By breaking the surface tension of the liquid on the substrate carrier, the liquid with particles drains (or "wicks") off of the substrate carrier more easily. Removing the liquid with particles from the substrate carrier tends to promote drying and rinsing of each of the substrates in a particle free manner.

The substrate support 249 provides lift and a contact point to each of the substrates 244 within the substrate carrier. To more easily appreciate the features of the substrate support, it should be noted that each of the substrates in a conventional substrate carrier touches the substrate carrier in at least three large regions. Each of the substrates is also relatively close to the insides of the substrate carrier. Accordingly, liquid easily accumulates and is often trapped on edges of each of the substrates.

To reduce this effect, the substrate support lifts the substrates in the substrate carrier by elevating each of the substrates in the carrier with a knife edge. By lifting each of the substrates in the substrate carrier, the substrate edges are further away from insides of the carrier, thereby allowing liquid to flow free from the region between the substrate edges and carrier insides. To further promote the removal of liquid from each of the substrates, the knife edge is preferably pointed, serrated, or any other shape that easily breaks the surface tension of the liquid at the bottom of each substrate. By breaking the surface tension of liquid at the substrate bottom edges, liquid flows free from the substrate bottom edges, thereby reducing the meniscus at such edges. The knife edge lifts each of the substrates at least 2 mm from the bottom insides of the carrier, and preferably lifts each of the substrates about 5 mm, but no more than about 20 mm. The substrate carrier support removes liquid such as water from the substrates, thereby decreasing the amount of water and in particular the particles in the water.

To add and drain liquid into the main chamber, and in particular the process region, the lower drain region 231 includes a fill inlet 232 and drain valve 236. The fill inlet provides liquid such as DI water and the like into the process region. The drain valve 236 removes liquid from the process region through the drain outlet 236. A plurality of drain holes 238 also exist at the bottom of the main chamber in the process region to distribute the liquid evenly therethrough. The lower drain region also includes an angled drain floor 237 at the bottom of the main chamber to facilitate liquid transfer, and a flat support surface 239 in the process region to support the substrate carrier support.

A cascade region 250 allows liquid to cascade out into cascade drain region 253. To rinse certain chemicals from the substrate carrier and substrates, ultra-purified DI water

enters through the fill inlet 237, rises through the drain holes 238, flows through the process region 240, and cascades over a partition 252 into the cascade drain region 253. This sequence of steps removes excess chemicals such as acids or the like from the substrate carrier and substrates, and also keeps such chemicals from accumulating in the main chamber and in particular the process region.

FIG. 4 illustrates a simplified front view of the cleaning chamber according to the present invention. For easy reading, FIG. 4 uses some of the same reference numerals as the FIG. 3 embodiment. The front-view embodiment shows elements such as the main chamber 210, the lid 220, the lower drain region 231, the process region 240, among others. The main chamber 210 includes the process region 240 and upper chamber region 215.

As shown, the substrate support 249 lifts each of the substrates from the substrate carrier to form a gap 260 between substrate edges and substrate carrier insides. The gap prevents liquid from accumulating between such substrate edges and substrate carrier insides. The gap is no greater than about 20 mm, but is larger than about 2 mm. The substrate support is a knife edge with triangular point 251. Other shapes may also be used to break the meniscus at the bottom of the substrate edges and remove water therefrom. The meniscus often forms at the bottom substrate and surface edges as liquid is being removed from the substrates. As previously noted, the meniscus often contains particles, often detrimental to the manufacture of an integrated circuit.

The front view also shows the substrate carrier supports 248. As shown, each of the substrate carrier support is arranged with different heights, typically lower to higher from one side of the process region to the other side of the process region. The different heights of the substrate carrier support tilt the position of the substrate carrier from horizontal. The tilt or angle of the substrate carrier also tilts the substrates, thereby preventing such substrates from sticking to each other during certain rinse and dry operations.

The front view further shows certain gas inlets 302, 304, and 306. Each of the gas inlets is a distribution plenum with a plurality of holes for distributing gas evenly over the process region. The embodiment includes two outside gas inlets 302 and 304, and a center carrier gas inlet 306. The two outside gas 302, 304 inlets generally introduce an ultra-pure non-reactive (e.g., non-oxidizing, non-reactive, inert, etc.) gas into the cleaning chamber. In some embodiments, the two outside gas inlets provide ultra-pure nitrogen to purge the main chamber from the environment, thereby creating an ultra-clean main process region, e.g., substantially free from particles. In these embodiments, the nitrogen gas (or absence of oxygen gas) is necessary or even critical to prevent the formation of oxidation on the substrate, e.g., semiconductor wafer, etc. The center gas inlet introduces the carrier gas comprising the cleaning enhancement substance. The non-reactive gas (or nitrogen) mixes with the carrier gas comprising cleaning enhancement substance in the cleaning chamber. By way of the ultra-pure non-reactive gas and carrier gas, the chamber is substantially free from particles greater than about 0.2 microns, and is preferably substantially free from particles greater than about 0.1 microns, thereby creating an ultra-pure and ultra-clean environment. Of course, the number of inlets and their use depend upon the particular application.

FIG. 5 is a simplified flow diagram 400 of an embodiment of a cleaning method according to the present invention. The rinse method is illustrated as a cleaning method for a recently wet etched substrate. The wet etched substrate for

illustrative purposes is etched in a solution of hydrofluoric acid (HF) or buffered hydrofluoric acid (BHF). Hydrofluoric acid is often used to remove oxides from surfaces of a semiconductor wafer. As merely an example, this embodiment should not be taken as limiting the scope of the present invention.

The flow diagram begins 400 by receiving a recently etched substrate (etched wafer) 410 from the BHF etch. The etched substrate has no oxide layer thereon from the BHF etch, and is predominately hydrophobic in characteristic. A step 420 of immersing the etched substrate in the bath of ultra-purified DI water follows. The etched substrate is immersed into the DI water from the acid bath in about 5.0 seconds or less, and preferably about 2.5 seconds and less.

The step of immersing the etched substrate immediately into the DI water substantially prevents formation of silicon dioxide from the oxygen in air, and promotes the formation of a thin but clean high grade silicon dioxide layer from the ultra-purified DI water. The DI water is substantially free from particles and therefore forms a substantially particle free silicon dioxide layer. The DI water can be at room temperature (e.g., 20° C.) or an elevated temperature, e.g., 25° C., 30° C., 40° C., 45° C., etc.

To remove acid such as the HF from the surface of the substrate, the ultra-purified DI water in the main chamber (or vessel) flows across the substrate and cascades over into a drain. The DI water cascade carries excess acid into the drain and reduces the acid concentration in the vessel.

Optionally, the DI water in the vessel may be removed by dumping it (step 440) into a bottom drain dump. Preferably, the dumping step is a partial dump, and not a complete dump or removal of DI water. During the removal of the DI water, an ultra-pure gas (non-reactive) replaces the DI water. A typical gas includes filtered nitrogen and others. The filtered gas also is ultra-clean, e.g., substantially free from particles.

After replacing the DI water with the clean gas, clean DI water from the DI water source flows into the main chamber to cover the surface area of the substrate. These aforementioned steps may be repeated (branch 445) alone or in any combination until substantially no residual acid exists (test 442) on the substrate.

When residual acid has been substantially removed from the substrate, a carrier gas, including a cleaning enhancement substance (e.g., trace amount of polar organic compound, helium, carbon dioxide, etc.), is introduced (step 450), and mixes with ultra-pure non-reactive gas and replaces the DI water. In one embodiment, the trace of polar organic compound in the gases includes a concentration ranging from about 1,000 ppm and less to about 500 ppm and less. The polar organic compound also can be at other concentrations, but is generally not saturated or superheated. The carrier gas is preferably ultra-pure nitrogen with a trace of polar organic compound such as isopropyl alcohol, di-acetone alcohol, 1-methoxy-2-propanol, and others. The carrier gas is also substantially free from particles of about 0.20 microns to about 0.15 microns, and is preferably free from particles of about 0.10 microns or less. For a typical batch of substrates in a conventional substrate boat, the amount of polar organic compound used is preferably less than a milliliter.

The trace of polar organic compound is made by bubbling carrier gas into a liquid solution of polar organic compound. In particular, the polar organic compound is made by flowing cold or hot nitrogen through a solution of polar organic compound at a rate of about 3 cubic feet/min. or less. The carrier gas comprising the polar organic compound then

mixes with either cold nitrogen at a flow rate of about 5 cubic feet/min. and less, or hot nitrogen at a flow rate of about 10 cubic feet/min. and less. A temperature of such hot nitrogen carrier gas is at about 70° F. and higher but not greater than 250° F., and is preferably about 185° F. and less. By mixing nitrogen gas with the carrier gas comprising the polar organic compound, the polar organic compound is substantially dilute (or a non-saturated vapor) in the main chamber.

The mixed carrier gas, including the polar organic compound and nonreactive gas, comes in contact with the attached DI water on the wafer, which is being drained off at a slow rate. This tends to remove particles from such substrate. A carrier gas, including isopropyl alcohol, 1-methoxy-2-propanol, di-acetone alcohol, or other polar organic solvents mixed with non-reactive gas, replaces the DI water at a rate of about 4 mm/second or less as measured from the substrate face, and is preferably at a rate of about 1 mm/second and less.

The trace of polar organic compound is believed to remove a substantial portion of the liquid on the substrate surface through a concentration gradient or mass transfer effect, e.g., Marangoni flow. This effect tends to increase the flow of liquid from the substrate surface through use of a solvent or any cleaning enhancement substance, but does not remove all liquid from the substrate surface. It is generally believed that the trace of polar organic compound in the gas changes the angle of the liquid meniscus on the substrate face to reduce surface tension of the liquid attached to the substrate face, thereby increasing fluid flow therefrom. It is also generally believed that the trace amount of the polar organic compound dopes the liquid attached to the substrate face to cause a concentration gradient of the polar organic compound in the attached liquid to accelerate fluid flow of the attached liquid off of the substrate face. In particular, the polar organic compound forms a concentration gradient along a boundary layer of liquid attached to the substrate surface, which facilitates the fluid flow therefrom. This fluid flow pulls or draws off any particles from the substrate face. These particles are less than about 0.5 microns in diameter or preferably 0.2 microns in diameter or more preferably 0.1 microns in diameter. Preferably, the carrier gas also is not heated but is at room temperature, e.g., 18° to 22.5° C.

In certain embodiments, a thin boundary layer of liquid still remains on the substrate face after liquid is removed from the chamber. This boundary layer often ranges from about 1,000 Å and less and is preferably 500 to about 50 Å, and is more preferably at about 100 Å and less. In one embodiment using isopropyl alcohol as the polar organic compound, the boundary layer is about 500 Å and less. In an embodiment using 1-methoxy-2-propanol, the boundary layer is about 100 Å and less. A further drying step can be used to evaporate such boundary layer.

In alternative embodiments, the gas (i.e., ultra-pure gas) is substantially free from any polar organic compounds, organic compounds, or the like. Like the previous embodiments, the gas replaces the DI water (step 450) being drained, removing water from the surface of the substrate, and also tends remove particles from such substrate via the DI water. The gas replaces the DI water at a rate of about 2.50 mm/second or less as measured from the substrate face, and is preferably at a rate of about 1.25 mm/second and less, and is more preferably at a rate of about 0.60 mm/second or less. In such embodiments, the present invention uses substantially no harmful solvents or the like, and is therefore even more safe, efficient, and economical.

A step of drying (step 460) is performed on the substrate and carrier for further drying, if necessary. The step of

drying substantially removes all liquid droplets adhering to surfaces such as substrate edges, carrier edges, and the like. In one embodiment, drying occurs by pulse flow drying. The step of pulse flow drying occurs by way of high velocity flow apparatus 600 illustrated in FIGS. 6, 6A, and 6B. The high velocity flow apparatus can be adapted into the present rinse chamber 200 among other systems. The high velocity flow apparatus includes a plurality of nozzles 601 directed over a substrate carrier 242. The substrate carrier 242 includes a plurality of substrates 244, each having residual amounts of liquid at their edges. Each substrate may have a liquid volume ranging from about 1.0 milliliter to about 0.2 milliliter but is preferably less than about 0.5 milliliter. The plurality of nozzles 601 is defined by a first set of nozzles 603 (first nozzle set), a second set of nozzles 605 (second nozzle set), and others.

The first nozzle set 603 is directed to the front side 607 of the substrates 244. The first nozzle set directs drying fluid at substrate edges 609 adjacent to the substrate carrier sides 246. The drying fluid can be any suitable fluid capable of removing liquid from the substrate edges and substrate surfaces. The drying fluid is preferably ultra-pure nitrogen and the like, but may also be a variety of other gases or gaseous mixtures. The first nozzle set preferably includes at least two nozzles, each placed at a location to direct drying fluid towards the substrate edges 609 adjacent to the substrate carrier sides. In the first nozzle set, a first nozzle A1 611 is directed to the substrate edges 609 at one side of the substrate carrier, and a second nozzle A2 615 is directed to the substrate edges 609 at the other side of the substrate carrier.

The second nozzle set 605 is directed to the back side 619 of the substrates 244. The second nozzle set directs drying fluid at substrate edges 609 adjacent to the substrate carrier sides 246. The second nozzle set preferably includes at least two nozzles, each placed at a location to direct drying fluid towards the substrate edges adjacent to the substrate carrier sides. In the second nozzle set, a first nozzle B1 621 is directed to the substrate edges at one side of the substrate carrier, and a second nozzle B2 625 is directed to the substrate edges at the other side of the substrate carrier.

The nozzle can be any suitable nozzle capable of enabling the drying fluid to flow over the substrate edges and remove liquid therefrom as illustrated by fluid flow distribution patterns in FIGS. 7 and 8. FIG. 7 illustrates a simplified side-view diagram of the apparatus of FIG. 6 according to the present invention. As shown, nozzles A1, A2, B2, and B3 direct drying fluid at the substrate edges (not shown) to preferably cover the inner surface area of the substrate carrier 242. Optionally, the apparatus can also include additional nozzles C1 and C2. Nozzles C1 and C2 are directed toward the substrate carrier front and back sides.

FIG. 8 illustrates a simplified front-view diagram of the nozzles A1 and A2 for the apparatus of FIG. 6 according to the present invention. Nozzles A1 and A2 direct drying fluid at the substrate edges along a front portion of the substrates. The nozzle is preferably narrow and long to produce a fluid flow at high velocity to cover the desired number of substrates. Each nozzle produces a fluid flow of, for example, nitrogen gas ranging from about 250 to about 350 standard cubic feet per hour, and is preferably about 300 standard cubic feet per hour. The pressure of the nitrogen gas at the nozzle opening ranges from about 80 to about 90 psia, and is preferably about 85 psia. A nozzle A1 also includes an opening 669 having a width of about 0.025 inch and a height of about 0.375 inch 673 as illustrated in FIGS. 6A and 6B. As shown, FIG. 6A illustrates a simplified cross-sectional



side view of the nozzle, and FIG. 6B illustrates a simplified cross-sectional front view of the nozzle. The nozzle opening 671 includes an angle  $\theta$  ranging from about 20 degrees to about 80 degrees, but is preferably about 75 degrees and less. The angle  $\theta$  may also be defined by a first angle  $\theta_1$  and second angle  $\theta_2$ . The first angle may be different from the second angle but can also be the same. Of course, other flow rates, pressures, and nozzle dimensions can be used depending upon the particular application.

Each nozzle is positioned to direct drying fluid to the substrate edges and portions of the substrate surface. The nozzle is directed to an inner edge of the substrate carrier to promote the removal of liquid between the substrate edges and the carrier sides. The nozzle is defined between about 0.5 inch to about 2 inches from an outside edge of the substrate carrier. The nozzle is placed at an angle from about 5° to about 85°, and is preferably about 45° from a line perpendicular from the substrate surface. Of course, the exact angle used depends upon the particular application.

Drying occurs by directing drying fluid from the first nozzle set and the second nozzle set in an alternating sequence against the substrate edges and portions of the substrate surfaces. For example, the first nozzle set sends a pulse of drying fluid against the substrate edges and portions of the front substrate surfaces, then the second nozzle set sends a pulse of drying fluid from the opposite direction against the substrate edges and portions of the back substrate surface. The drying fluid pulses from the first nozzle set and the second nozzle set alternate until no more liquid remains on the substrate edges.

In removing water from the substrate edges, the second nozzle set has a pulse duration which is longer than the pulse duration of the first nozzle set. Water adheres on the back-side of the substrate and substrate edges on a conventional semiconductor wafer with a greater attractive force than the front-side of the substrate. Accordingly, it is often preferable to have a pulse duration at the second nozzle set which is at least two times longer than the pulse duration at the first nozzle set. The pulse duration at the second nozzle set can also be three times longer or more than the pulse duration at the first nozzle set. The pulse duration for the first nozzle set ranges from about 1 to 3 seconds and greater, and the pulse duration for the second nozzle set ranges from about 2 to 6 seconds and greater. The number of pulses is preferably greater than 5 for each substrate side for a total of about 30 seconds of total pulsing time. Of course, other selected pulses among the first and second nozzle sets may also be performed, depending upon the particular application.

Optionally, pulse flow drying is followed by flowing hot nitrogen gas over the substrate carrier (step 470). The hot nitrogen gas is ultra-pure nitrogen gas with a temperature at about 70° F. and is preferably greater than 150° F., but no greater than 200° F. The combination of hot nitrogen and pulse flow drying reduces actual drying time by about one half, as compared to drying solely by means of hot nitrogen and the like. Alternatively, a drying gas such as nitrogen can be used alone to dry the wafer. Of course, other carrier gases and combinations thereof may also be used depending upon the particular application.

FIG. 9 is a simplified diagram of an alternative embodiment of the high velocity flow apparatus 900 according to the present invention. The high velocity flow apparatus includes a plurality of nozzles 901 directed over a substrate carrier 242. The substrate carrier 242 includes a plurality of substrates 244 (not shown), each having residual amounts of liquid at their edges. Each substrate may have a liquid

volume ranging from about 1.0 milliliter to about 0.2 milliliter but is preferably less than about 0.375 milliliter. The plurality of nozzles 901 is defined by a first set of nozzles 903 (first nozzle set), a second set of nozzles 905 (second nozzle set), a third set of nozzles 907 (third nozzle set), a fourth set of nozzles 909 (fourth nozzle set), and others.

The nozzles are placed at selected locations surrounding the substrate carrier, and in particular the substrates disposed in the substrate carrier. The first nozzle set A1, A2 is placed at an end 908 of the substrate carrier facing the substrate faces, and the second nozzle set B1, B2, is placed at the other end 910 of the substrate carrier facing the back-side of the substrates. The third nozzle set includes nozzles A3, A4 which face each other and are disposed adjacent to a first portion 911 of the substrate carrier edges. The fourth nozzle set includes nozzles B3, B4 also face each other and are disposed adjacent to a second portion 913 of the substrate carrier edges. The design of each nozzle is similar to the previous embodiment, but each nozzle covers less area than the previous embodiment.

In removing residual water from the substrates, each set of nozzles is pulsed in a selected pattern. For example, the pulse pattern begins by pulsing drying fluid at nozzles A1, A2 followed by nozzles A3, A4 followed by nozzles B1, B2 followed by nozzles B3, B4, and the sequence repeats as often as it is necessary to remove substantially all water from the substrate. Alternatively, the pulse pattern begins at nozzles B3, B4 followed by nozzles B1, B2 followed by nozzles A3, A4 followed by nozzles A1, A2, and the sequence then repeats as often as it is necessary to remove substantially all water from the substrate.

Optionally, the pulse drying is followed by flowing hot nitrogen gas over the substrate carrier. The hot nitrogen gas is ultra-pure nitrogen gas with a temperature at about 70° F. and is preferably greater than 150° F., but no greater than 200° F. The hot nitrogen gas flows over the substrates for a period of time of at least 30 seconds and more, or preferably 50 seconds and more. The combination of hot nitrogen and pulse drying reduces actual drying time by about one half, as compared to drying solely by means of hot nitrogen and the like. The pulse drying step removes or evaporates liquid from the boundary layer. Pulse drying also removes or evaporates liquid on edges of the substrate. Alternatively, hot nitrogen gas alone can be used to dry the wafer. Of course, other carrier gases and combinations thereof may also be used depending upon the particular application.

Another method to rinse and dry HF etched substrate includes a selected sequence of the aforementioned steps. A solution of HF etches silicon dioxide off the semiconductor substrate. To stop etching, the substrate is quickly immersed into ultra-pure DI water in a vessel. After immersing the etched substrate into the DI water, the vessel is purged with filtered nitrogen gas. The nitrogen gas flows at a rate of ranging from about 1 cubic feet/min. to about 10 cubic feet/min., and is preferably at about 2 cubic feet/min.

To further rinse and remove acid from the substrate, DI water flows past the substrate and cascades from a top portion of the vessel into a drain to cascade rinse the substrate. A quick dump follows the cascade rinse. Preferably, the quick dump occurs at a rate where the liquid level drops at a rate greater than about 20 mm/sec. as measured from a substrate face. During the quick dump, clean nitrogen gas replaces the DI water, thereby preventing any oxidation of the substrate from air. Clean DI water fills the vessel and replaces the nitrogen to re-immerses the substrate in the DI water.

A combination of a carrier gas, including a cleaning enhancement substance, mixed with ultra-pure non-reactive gas then slowly replaces the DI water to remove substantially all acid off the substrate. The slow replacement step substantially eliminates any water from the substrate edges (a meniscus). After another sequence of quick DI water fills and partial dumps, another gaseous mixture, including carrier gas and cleaning enhancement substance, replaces the DI water. Substantially, all water is removed from the substrate at this time. The cleaning enhancement substance reduces the surface tension of the liquid on the substrate to enhance fluid flow therefrom. During removal of the liquid, it pulls particles off the substrate surfaces, thereby cleaning the substrate. To further dry the substrate and carrier, warm or hot nitrogen is pulsed into the vessel. The nitrogen includes a temperature ranging from about 70° F. to about 250° F.

As previously noted, alternative embodiments use a gas without any polar organic compound or the like to replace the DI water. In such embodiments, the gas replaces the DI water at a rate of about 2.50 mm/second or less as measured from the substrate face, and preferably at a rate of about 0.80 mm/second or less. The gas without any polar organic compounds or the like may also be nitrogen at a temperature ranging from about 70° F. to about 250° F. To further dry the substrate and carrier, warm or hot nitrogen is pulsed into the vessel. The nitrogen includes a temperature ranging from about 70° F. to about 250° F.

The aforementioned methods also include the use of a certain substrate support and a substrate carrier support to enhance wicking or to draw liquid away from the substrate and carrier. For example, the substrate support includes a knife edge that lifts the substrates to prevent accumulation of water at the substrate edges, and in particular the substrate bottom edges. The substrate carrier support wicks or draws the water from the surface of the substrate carrier, and also puts a slight tilt from horizontal on such carrier.

The slight tilt of the substrate carrier also tilts the substrates, which tends to prevent them from sticking to each other. As previously noted, sticking substrates often accumulate water therebetween. The accumulation of water also accumulates particles, which may be in the water. By removing the water and particles from the substrate, the present method provides higher device yields on a typical semiconductor substrate.

FIGS. 10A–10B are simplified cross-sectional view diagrams of a substrate carrier 1000 according to the present invention. This substrate carrier is for a disk 1001 or the like. The substrate carrier includes a lower support beam 1005, an upper support beam 1003, and a plurality of center support beams 1011, 1013, and 1015. The support beams support or hold the disk 1001 in its place. The disk is often a flat circular shaped article with an opening in its center region. The disk can be made of almost any type of material such as metal, plastic, and others. This disk has an inner periphery 1009, an outer periphery 1007, a face 1008, and other elements. In this embodiment, the inner periphery 1009 and the outer periphery 1007 are circular in shape. But the shape also can be square, rectangular, or the like. The face is substantially flat, but may also have small ridges thereon. In certain embodiments, the face can be porous.

The support beams also have knife edges 1017 that draw fluid or liquid away from the disk by breaking the surface tension of the fluid or liquid attached to the disk. Typically, the fluid or liquid accumulates along edges of the inner and

outer periphery. The support beams are located surrounding the periphery of the disk to draw fluid evenly from the disk. Preferably, the support beams are spaced apart from each other at a relatively equal distance.

The center support beams are illustrated by FIG. 10B. The center support beams include the upper center support beams 1013, 1015, and the lower center support beam 1011. Preferably, each of the support beams has a knife edge 1017 or ridges thereon. The ridges have outer bevelled portions 1021, 1023, a lower center portion 1025, and a higher center portion 1027. Preferably, the lower center portion is defined at a lower region where the bevelled portions meet. The upper center portion is defined at a higher region where the bevelled portions meet. An angle  $\theta_1$  defining the lower center portion between the bevelled portions ranges from about 85° to about 150°, and is preferably about 90° to about 120°. An angle  $\theta_2$  defining the upper center portion between the bevelled portions ranges from about 85° to about 150°, and is preferably about 90° to about 120°. The angles  $\theta_1$ ,  $\theta_2$  are selected to draw liquid or fluid away from the disk, thereby enhancing fluid flow or drying.

One of the center support beams is adjustable in the y-direction. In this embodiment, the upper center support beam 1015 adjusts its location along the y-axis. This adjustment also allows the upper center support beam to firmly engage and hold the inner periphery 1009 of the disk 1001. Engagement of the center support beams onto the inner periphery of the disk draws residual fluid on edges of the inner periphery along each center support beam. Preferably, the upper center support beam is also adjustable in the x-direction. More preferably, each of the center support beams is adjustable in both the x-direction and the y-direction in the same plane. This adjustment allows for the center support beams to engage with the inner periphery of the disk.

The center support beam can be made of any suitable material, but its surface is preferably hydrophilic to draw water away from the disk (refer to arrows). The surface can be made of metal such as stainless steel, steel alloys, or others. The surface also can be made of plastics, glass, quartz, or the like. The material needs to have sufficient strength for durability, chemical resistance, and structural integrity. Of course, the type of material used and its surface depend upon the application.

FIGS. 11A–11F are simplified diagrams of a further alternative embodiment 1100 of a substrate carrier according to the present invention. FIG. 11A is a side-view diagram of the substrate carrier 1100. The substrate carrier includes a plurality of walls 1101 and a plurality of substrates 1102 disposed therebetween. The substrates can be almost any type of substrate such as a semiconductor wafer or the like. Of course, the type of substrate used depends upon the particular application. Generally, fluid accumulates on edges of the substrate after cleaning or removing liquid from the substrate surfaces.

A plurality of lower substrate supports 1106, 1108, and an upper substrate support 1104 are also shown. Each of the substrate supports has knife edges 1107 engaged along the substrates' edges, which are used to draw fluid or liquid from the substrate edges. As previously noted, the knife edges break the surface tension of the fluid on the substrate edges, and draw such fluid often with particles therefrom. This tends to remove residual or unwanted fluid from the substrate, and in particular the substrate edges.

A front-view diagram of the substrate carrier 1100 is shown by FIG. 11B. The front-view diagram includes the

substrate 1102 having a face 1112 and substrate edges 1111 (or an outer periphery). Three lower substrate supports 1106, 1108 are located near the bottom portion of the substrate 1102. Lower substrate support 1106 is located at a center bottom portion of the substrate, and is perpendicular to the x-direction. Lower substrate supports 1108 are located perpendicular to the x-direction at an upper bottom portion of the substrate. These substrate supports are disposed along the bottom surface of the substrate to support such substrates, and draw any residual liquid from the substrate edges. The upper substrate support 1104 is disposed perpendicular to the x-direction, and engages with an upper center portion of the substrate. Preferably, the upper center portion is in-line in the y-direction with lower substrate support 1106, but also can be at other locations. Preferably, the upper substrate support 1104 firmly engages with the upper center portion of the substrate. This upper substrate support 1104 breaks the surface tension of fluid on the substrate edges, and draws such fluid off, thereby enhancing substrate drying.

FIGS. 11C and 11D illustrate a top-view diagram of the substrate carrier and a bottom-view diagram of the substrate carrier, respectively. As shown, the upper substrate support 1104 is located overlying a center portion of the substrates along the z-direction. Bottom substrate supports 1106, 1108 run parallel to each other in the z-direction. These substrate supports also are spaced evenly among each other. Alternatively, the upper substrate support and bottom substrate support also can be at other locations.

FIGS. 11E and 11F illustrate an example of a substrate support according to the present invention. This substrate support can be any of the above substrate supports 1104, 1106, and 1108. The substrate support 1117 includes a notched portion which engages with a side 1115 of the substrate carrier. This notched portion on the substrate support can be adapted to any conventional substrate carriers for use with the present invention. Engagement between the substrate support 1117 and the side 1115, however, also can occur using other techniques such as welding, bonding, or other engagement means.

The substrate support can be made of any suitable material, but its surface is preferably hydrophilic to draw water away from the substrate (refer to arrows). The surface can be made of metal such as stainless steel, steel alloys, or others. The surface also can be made of plastics, glass, quartz, or the like. The material needs to have sufficient strength for durability, chemical resistance, and structural integrity. Of course, the type of material used and its surface depend upon the application.

Each of the support beams has a knife edge 1107 or ridges thereon. The ridges have outer bevelled portions 1121, 1123, a lower center portion 1125, and a higher center portion 1127. Preferably, the lower center portion is defined at a lower region where the bevelled portions meet. The upper center portion is defined at a higher region where the bevelled portions meet. An angle  $\theta_1$  defining the lower center portion between the bevelled portions ranges from about 85° to about 150°, and is preferably about 90° to about 120°. An angle  $\theta_2$  defining the upper center portion between the bevelled portions ranges from about 85° to about 150°, and is preferably about 90° to about 120°. The angles  $\theta_1$ ,  $\theta_2$  are selected to draw liquid or fluid away from the disk, thereby enhancing fluid flow or drying.

In addition, the aforementioned cleaning method occurs without movement of the substrate. In fact, the substrate carrier remains substantially stationary after being immersed, and during the drying, cascade rinse, and other

steps. By way of less movement, the system has fewer mechanical parts and is often easier to use and maintain than certain prior art systems.

Moreover, the amount of polar organic compound used for each batch of substrates is typically less than a fraction of a milliliter. The use of less organic compounds is often advantageous to the highly flammable prior art methods of drying a substrate by way of IPA for example. In certain embodiments, no polar organic compounds or the like are used. Accordingly, the present method is less hazardous than certain prior art methods to both health and environment.

The aforementioned embodiments also are used in other selected semiconductor fabrication process steps. In one embodiment, the cleaning technique occurs in pre-gate oxide cleans. Pre-gate oxide cleans were generally not performed due to the sensitivity of gate oxide layer formation. That is, convention pre-gate oxide cleans were not performed due to the introduction of particles onto the semiconductor substrate. The present technique, however, actually removes any particles that may remain on the surfaces of the substrate before gate oxide layer formation, thereby improving the general quality of the gate oxide layer. The present technique removes substantially all particles greater than about 0.5 microns, and preferably 0.2 microns, and more preferably 0.1 microns.

In an alternative specific embodiment, the present cleaning technique can be applied before other semiconductor process applications. These process applications are described in great detail in a text written by Stanley Wolf and Richard N. Tauber, *Semiconductor Processing For The VLSI Era, Vol. 1: Process Technology* (1986) (herein "WOLF"). For example, the present technique is applied as a pre-epitaxial, pre-diffusion, pre-metal, pre-poly, pre-implant, pre-photoresist, and pre-stack oxide cleaning techniques. Generally, the present cleaning technique can be applied at room temperature with trace quantities of polar organic compound. The trace quantity of polar organic compound at room temperature does not generally detrimentally influence the semiconductor or photoresists. As noted in the background of invention, photoresists often dissolve during high temperature processing using solvents. As also previously noted, the present technique actually removes particles, rather than introducing them.

In an alternative embodiment, the present cleaning technique can be applied after performing a selected semiconductor fabrication process. An example of this fabrication process includes nitride deposition, polish cleans (e.g., CMP), buffered oxide etches, and metal deposition. These process steps also are described in great detail in a text written by WOLF. Additional applications of the present cleaning technique also can be applied for hydrofluoric acid last recipes and critical metal oxide silicon etches. As previously noted, the present technique actually removes particles from the semiconductor, rather being another process that introduces them.

#### Experiments

To prove the principle and demonstrate the operation of the present method and apparatus, experiments were performed.

In these experiments, a 6-inch silicon wafer was used as a substrate. The 6 inch silicon wafer included an overlying layer of high quality silicon dioxide, typifying a recently HF etched wafer with an overlying oxide layer. The 6-inch silicon wafer was placed in a wafer carrier, which was immersed into a bath of rinse water in a vessel. In the vessel, the 6-inch silicon wafer was at a substantially vertical position, that is, faces of the wafer were substantially normal

to the water level. The water is standard rinse water and included a resistance of about 17 megohms, and had a temperature of about 70° F. In the immersed position, the wafer was substantially wet.

To dry the wafer, water was drained from the bottom of vessel. The water level was substantially normal to the wafer faces. The water was drained at a substantially constant rate from the bottom of the vessel. During the draining step, the wafer remained substantially motionless.

By way of an adjustable outlet valve at the drain, a different drain speed in multiple runs was used to determine the particular drain rates at which drying occurred more effectively. Drain speed is measured by the amount of time necessary to drain the water from the vessel in terms of decreasing water level measured in millimeters per second (mm/sec.).

FIG. 12 illustrates a "drying effectiveness" as a function of drain speed (in millimeters per second). The drying effectiveness is a surface area percentage of the wafer without water residue, measured as a percentage. The surface area of the wafer includes the faces and wafer edges. As noted above, it is quite important to remove all water from the wafer which often includes a meniscus at the wafer edges. As shown, the drying effectiveness in this experiment is a non-linear function with respect to drain speed. For example, the drying effectiveness of the sample wafer is about 99.0% at a drain speed of about 2.5 mm/sec. A drain speed of about 1.25 mm/sec. has a drying effectiveness of about 99.8%. A drying effectiveness of about 100% (or completely dry wafer excluding wafer edges) was produced with a drain speed of about 0.83 mm/sec. and less. Any residual water on the wafer edges was removed by hot dry nitrogen being introduced for about 2 minutes or less.

This experiment shows that a substantially clean and dry wafer may be produced by way of an embodiment of the present process. This present process does not rely upon any potentially harmful organic solvents or the like. In addition, the present process provides a substantially clean and dry wafer without mechanical movement of the wafer thereby decreasing the possibility of any mechanical damage of the wafer loss due to machine malfunction. Furthermore, the substantially wafer may be provided without the use of a heater or heating element, thereby decreasing hazards of fire and such. Accordingly, this experiment shows a safe, efficient, and easy method of drying and cleaning a wafer according to the present invention.

While the above is a full description of the specific embodiments, various modifications, alternative constructions, and equivalents may be used. For example, while the description above is in terms of a method and apparatus for semiconductor substrates, it would be possible to implement the present invention to the manufacture of raw wafers, disks and heads, flat panel displays, microelectronic masks, and other applications requiring high purity wet processing such as steps of rinsing, drying, cleaning, and the like. In addition, the systems of FIGS. 1-5 are in terms of a cleaning system for semiconductors. A skilled artisan may, alternatively, employ such systems to other industries such as electrochemical, pharmaceutical, printed circuit board, optical devices, and any other industry that needs an improved technique to rinse and dry an article of manufacture. Furthermore, the apparatus of FIGS. 6-11F are in terms of the present cleaning system, but also can be employed in any other cleaning system, drying system, rinse system, or the like.

Therefore, the above description and illustrations should not be taken as limiting the scope of the present invention which is defined by the appended claims.

What is claimed is:

1. Apparatus for holding a plurality of substrates, said apparatus comprising:

a lower support, said lower support comprising a plurality of first ridges, one of said first ridges providing a support for a lower substrate portion;

a center support, said center support comprising a plurality of third ridges, one of said third ridges providing a support for a center substrate portion; and

an upper support, said upper support comprising a plurality of second ridges, one of said second ridges providing a support for an upper substrate portion;

wherein said lower substrate portion, said center substrate portion, and said upper substrate portion are defined on a substrate; and

wherein said one first ridge, said one second ridge, and said one third ridge, can draw a portion of liquid from said substrate.

2. Apparatus of claim 1 wherein said one of said first ridges and said one of said second ridges comprise a bevelled portion, said bevelled portion meeting at a lower center portion and an upper center portion.

3. Apparatus of claim 1 wherein said lower substrate portion is a lower edge of said substrate.

4. Apparatus of claim 1 wherein said upper substrate portion is an upper edge of said substrate.

5. Apparatus of claim 1 wherein said substrate is a disk.

6. Apparatus of claim 5 wherein said disk is made of a material selected from a metal or a plastic.

7. Apparatus of claim 5 wherein said disk has a substantially flat face.

8. Apparatus of claim 5 wherein said disk is circular in shape, said disk comprising a center opening coupled to said center substrate portion.

9. Apparatus of claim 1 wherein said substrate comprises a face, said face being porous.

10. Apparatus of claim 1 wherein one of said third ridges comprises an outer bevelled portion.

11. Apparatus of claim 1 wherein one of said third ridges comprises a lower center portion and an upper center portion.

12. Apparatus of claim 1 wherein one of said third ridges comprises a pair of outer center portions, a lower center portion, and an upper center portion, said upper center portion being defined at a higher region where said pair of outer center portions meet.

13. Apparatus of claim 1 wherein one of said third ridges comprises a lower center portion between a pair of bevelled portions, said lower center portion being defined between said pair of bevelled portions at an angle ranging from about 85 to about 150 degrees therebetween.

14. Apparatus of claim 1 wherein one of said third ridges comprises a lower center portion between a pair of bevelled portions, said lower center portion being defined between said pair of bevelled portions at an angle ranging from about 90 to about 120 degrees.

15. Apparatus of claim 1 further comprising an upper center support beam, said upper center support firmly engaging an inner periphery of said substrate.

16. Apparatus of claim 15 wherein said upper center support beam is adjustable in a vertical direction.

17. Apparatus of claim 15 wherein said upper center support beam is adjustable in a horizontal direction.

18. Apparatus of claim 1 wherein at least one of said supports is made from a material selected from a plastic, a glass, quartz, stainless steel, and steel alloys.

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19. Apparatus for processing an object, said processing apparatus comprising a device for holding a plurality of objects, said device comprising:

a lower support, said lower support comprising a plurality of first ridges, one of said first ridges providing a support for a lower object portion of an object, said one first ridge providing said support drawing a first portion of liquid from said lower object portion; and

a center support, said center support comprising a plurality of third ridges, one of said third ridges providing a support for a center object portion of said object, said third ridge providing said support drawing a third portion of liquid from said center object portion.

20. Apparatus of claim 19 wherein said device further comprising an upper support, said upper support comprising a plurality of second ridges, one of said second ridges providing a support for an upper object portion of said object, said upper support providing said support drawing a third portion of liquid from said object.

21. Apparatus of claim 20 wherein said upper object portion is an upper edge of said object.

22. Apparatus of claim 20 wherein said object is a disk.

23. Apparatus of claim 22 wherein said disk is made of a material selected from a metal or a plastic.

24. Apparatus of claim 22 wherein said disk has a substantially flat face.

25. Apparatus of claim 22 wherein said disk is circular in shape, said disk comprises a center opening.

26. Apparatus of claim 19 wherein one of said first ridges and one of said second ridges comprise a bevelled portion, said bevelled portion meeting at a lower center portion and an upper center portion.

27. Apparatus of claim 19 wherein said object comprises a face, said face being porous.

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28. Apparatus of claim 19 wherein one of said third ridges comprises an outer bevelled portion.

29. Apparatus of claim 19 wherein one of said third ridges comprises a lower center portion and an upper center portion.

30. Apparatus of claim 19 wherein one of said third ridges comprises a pair of outer center portions, a lower center portion, and an upper center portion, said upper center portion being defined at a higher region where said pair of outer center portions meet.

31. Apparatus of claim 19 wherein one of said third ridges comprises a lower center portion between a pair of bevelled portions, said lower center

32. Apparatus of claim 19 wherein one of said third ridges comprises a lower center portion between a pair of bevelled portions, said lower center portion being defined between said pair of bevelled portions at an angle ranging from about 85 to about 150 degrees.

33. Apparatus of claim 19 wherein one of said third ridges comprises a lower center portion between a pair of bevelled portions, said lower center portion being defined between said pair of bevelled portions at an angle ranging from about 90 to about 120 degrees.

34. Apparatus of claim 19 wherein said device further comprises an upper center support beam, said upper center support being firmly engaging an inner periphery of said object.

35. Apparatus of claim 34 wherein said upper center support beam is adjustable in a vertical direction.

36. Apparatus of claim 34 wherein said upper center support beam is adjustable in a horizontal direction.

37. Apparatus of claim 19 wherein at least one of said supports is made from a material selected from a plastic, a glass, quartz, stainless steel, and steel alloys.

\* \* \* \* \*

**United States Patent** [19]  
**Maeda et al.**

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[45] **Date of Patent:** May 24, 1988

[54] **TREATMENT METHOD FOR  
PLATE-SHAPED SUBSTRATE**

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Jan. 17, 1986 [JP] Japan ..... 61-8209  
Jan. 17, 1986 [JP] Japan ..... 61-8210

[51] **Int. Cl.<sup>4</sup>** ..... H01L 21/306; B44C 1/22;  
C03C 15/00; C03C 25/06

[52] **U.S. Cl.** ..... 156/637; 134/32;  
134/34; 156/643; 156/646; 156/653; 156/657;  
156/659.1; 156/662; 156/345

[58] **Field of Search** ..... 156/637, 638, 639, 646,  
156/648, 643, 653, 657, 659.1, 662, 345; 134/32,

34

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[57] **ABSTRACT**

A treatment method for plate-shaped substrate capable of uniformly performing the treating operation, performing a large amount of treatment, and facilitating the automation of the work independently of the surface nature of the substrate such as base plates of Si wafer for integrated circuit manufacturing use. The method is achieved by making it easier for the whole substrate surface to be wetted with the treatment liquid, through exposing the substrate to liquid or gas material which is soluble mutually with a treatment liquid prior to treatment with the treating liquid, to avoid treatment and thus uneven treatment to improve the yield.

17 Claims, 2 Drawing Sheets

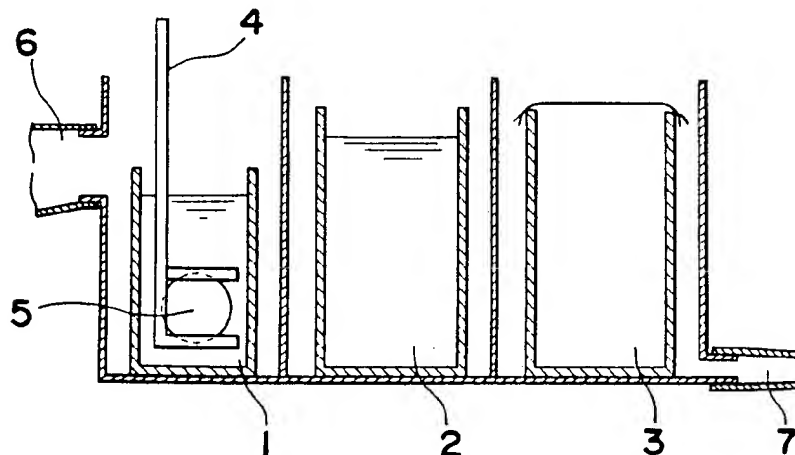


Fig. 1

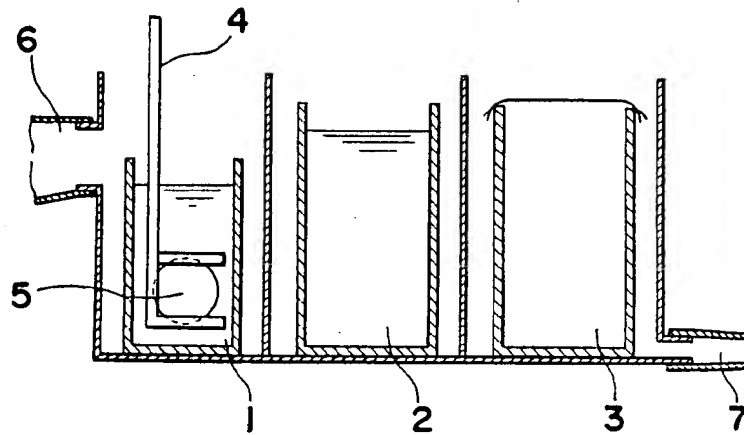


Fig. 2

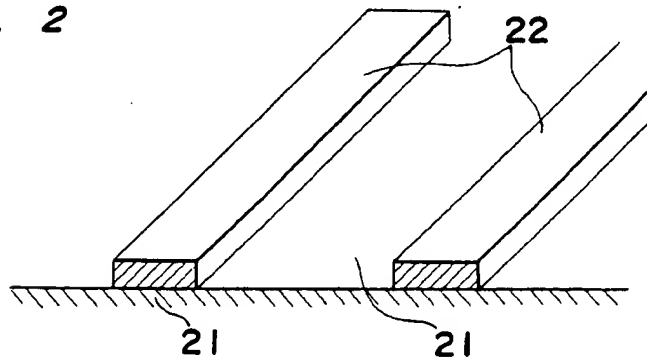


Fig. 3

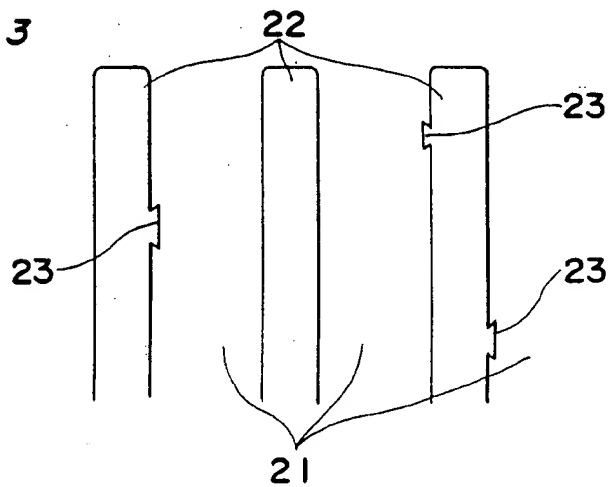


Fig. 4

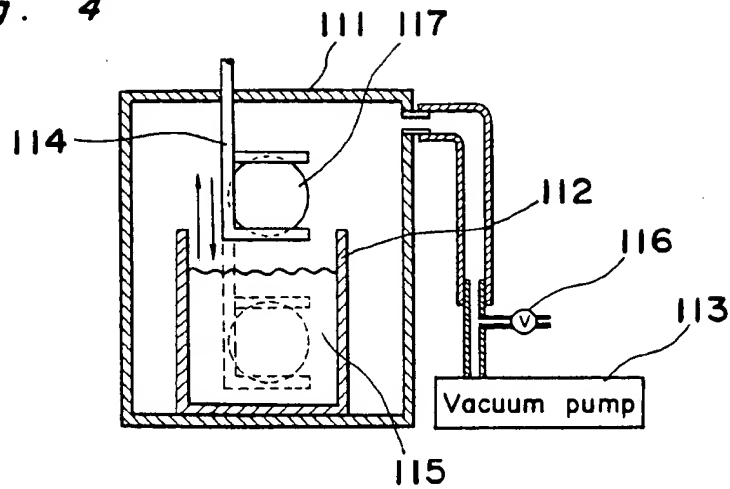


Fig. 5

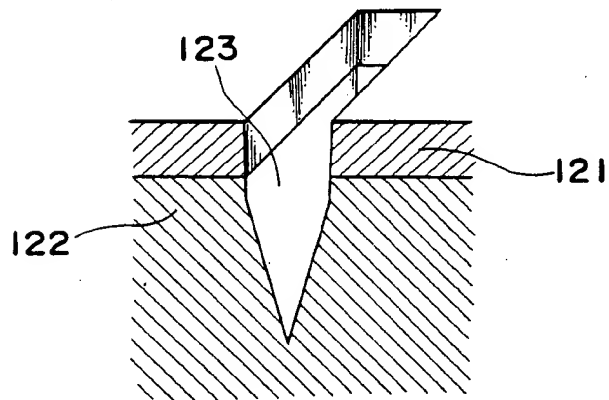
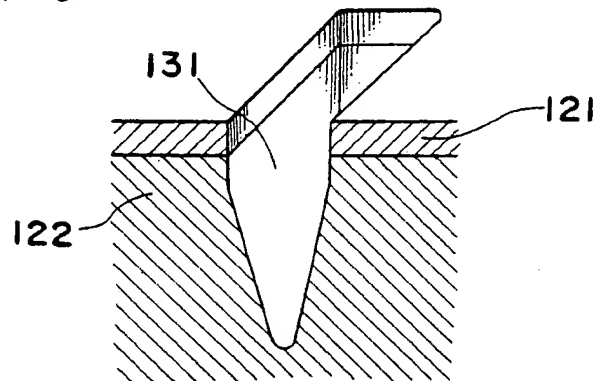


Fig. 6





## TREATMENT METHOD FOR PLATE-SHAPED SUBSTRATE

### BACKGROUND OF THE INVENTION

The present invention relates to a treatment method which makes it possible to perform the uniform treatment of a plate-shaped substrate, which has fine unevenness upon the surfaces represented for instance, a base plate for integrated circuit (IC) manufacturing use, a disc plate for image recording use, and a base plate for liquid-crystal display use when the surface treatment such as washing, etching, fat removing, resist friction or the like is applied by the use of the various kinds of liquid chemicals (hereinafter referred to as treatment liquid).

By way of example, in the following detailed description, the etching and washing of the base plate for IC manufacturing use (hereinafter referred to as Si wafer) which demands the uniformity and washing degree of the treatment particularly in these fields will be described.

The conventional etching methods of Si wafer are

The conventional etching methods of Si wafer are as follows.

1. A method of being dipped in the etching liquid (hereinafter referred to as a first method).

2. A method of jetting the etching liquid from the nozzles, rotating the Si wafer (as described within Japanese Patent Application publication (unexamined) Tokkaisho No. 53-8577, Japanese Patent Application Publication (unexamined) Tokkaisho No. 54-7874, Japanese Patent Application Publication (unexamined) Tokkaisho No. 56-27931, Japanese Patent Application Publication (unexamined) Tokkaisho No. 58-122732, Japanese Patent Application Publication (unexamined) Tokkaisho No. 58-196024, Japanese Patent Application Publication (unexamined) Tokkaisho No. 59-103344, Japanese Patent Application Publication (unexamined) Tokkaisho No. 59-204238) (hereinafter referred to as a second method).

3. A method of performing an etching method under the reduced pressure (as disclosed in the Japanese Patent Application Publication (examined) Tokkoshu No. 60-7382) (hereinafter referred to as a third method).

Also, as the method of washing the Si wafer, existing circumstances are that the washing operation is performed by the joint use of auxiliary means for oscillating the Si wafer with most of the Si wafer being dipped in the washing liquid, or for applying the ultrasonic waves.

However, the conventional art has the following problems in the treatment such as washing or etching.

1. In the above-described first method, air is attached on the corner portion of the pattern or in the small indentation formed on the Si wafer surface to prevent the Si wafer from coming into contact against the treatment liquid to cause the uneven treatment.

Particularly, when the hydrophilic portion of the  $\text{SiO}_2$  film or the like, and the hydrophobic portion of Si, Si film nitride or the like are mixed on the Si wafer surface, the bubbles are likely to be attached onto the boundary line therebetween to often cause the uneven treatment.

Also, the air contained in the contact hole for wiring use or in the trench formed on the Si is not easy to

eliminate, and the treatment thereof cannot be applied into the contact hole or the trench.

2. As the treatment liquid of the above-described second method has kinetic energies, the air bubbles are generally likely to be somewhat removed more than the first method. However, air-bubbles are often caused (especially when the hydrophobic portion exists therein) all the more, because the bubbles are caused when the treatment liquid collides with the Si wafer.

Also, even in the second method, the effects are hardly provided in the removing operation of the air bubbles within the contact hole or the trench to cause the uneven treatment. Furthermore, the treatment liquid is likely to be scattered in all directions to cause a problem in the operation safety. 3. As gas to be caused by the etching reaction is removed in the above-described third method, the etching chamber is normally kept under the reduced condition during the treatment of the Si wafer. However, in the treatment where the gas is not caused through the reaction as in the etching of, for example,  $\text{SiO}_2$  with fluoric acid or in the etching of Si of the Si nitride with phosphoric acid, the large air bubbles attached when the Si wafer has been dipped in the treatment liquid are inflated further by the reduced pressure to provide the sufficient buoyance so that the large bubbles are disconnected from the wafer surfaces. However, the small air bubbles cannot get sufficient buoyance for disconnection if they are inflated, and, then, they remain attached on the Si wafer surfaces as large bubbles during the pressure-decreasing time. The volume of the air bubbles is inflated unexpectedly 25.3 times as much under the decreased pressure of, for example, 30 Torr. Even the air bubbles of such size as may be neglected under the atmospheric pressure have large influences upon the uneven etching applied on the Si under the decreased pressure to deteriorate the uniformity. In addition, acid corrosion gas such as HF or the like is produced in large amount so as to normally retain the decreased pressure, which causes not only further corrosion of the pressure decreasing apparatus such as rotary pump or the like, but also shortens the service life of the pressure decreasing apparatus.

### SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a treatment method for a plate-shaped substrate which is capable of uniformly performing the treating operation, performing a large amount of treatment, and facilitating the automation of the work independently of the surface nature of a substrate to be treated such as Si wafer or the like.

Another object of the present invention is to provide a treatment method for a plate-shaped substrate which is achieved by making it easier for the whole treated substrate to be wet with the treatment liquid, through exposing the substrate to a liquid or gas material which is mutually soluble with the treatment liquid, prior to treating the substrate with the treatment liquid, to avoid the uneven treatment thereof, thereby to improve the yield.

Namely, for accomplishment of the above objects, the present invention provides a treatment method of dipping a substrate to be treated such as a plate in treatment liquid to apply the treatment after the substrate has been exposed to a liquid or gas of a material which is mutually soluble with the treatment liquid, and thereafter removing the treatment liquid and attached to the treated substrate efficiently.

Also, the present invention includes a treatment method of decreasing the pressure within a container, after a substrate to be treated has been brought into treatment liquid within the container provided with means for decreasing the pressure therein, to restore the pressure to the atmospheric pressure again, thereafter completing the treatment to remove the treatment liquid attached on the treated substrate.

Furthermore, the present invention includes a treatment method of decreasing the pressure within a container, after the liquid which is soluble with treatment liquid has been brought into contact against a substrate to be treated within the container provided with means for decreasing pressure therein, to restore the pressure to the atmospheric pressure, thereafter bringing the treated substrate into contact against the treatment liquid to complete the treatment, and, then, removing the treatment liquid attached on the treated substrate.

Also, the present invention includes a treatment method of separately placing a substrate to be treated and treatment liquid within a container provided with means for decreasing the pressure therein to decrease the pressure within the container to remove gas on the surfaces of the substrate, thereafter restoring the pressure located within the container to the atmospheric pressure after the substrate has been brought into contact against the treatment liquid under the decreased pressure, thereafter removing the treatment liquid attached on the treated substrate.

Also, the present invention includes a treatment method of individually placing a substrate to be treated and liquid soluble with treatment liquid respectively within a container provided with an apparatus for decreasing the pressure therein, restoring the pressure provided within the container to the atmospheric pressure, after the substrate has been brought into contact against the liquid soluble with the treatment liquid under the decreased pressure, to apply the treatment upon the substrate with the treatment liquid, thereafter removing the treatment liquid attached on the treated substrate.

#### BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and features of the present invention will become apparent from the following description taken in conjunction with the preferred embodiments thereof with reference to the accompanying drawings, in which:

FIG. 1 and FIG. 4 are cross-sectional views of a treating apparatus to be used in the embodiment of the treatment method of the present invention;

FIG. 2 is a perspective view with the line shaped pattern of the  $\text{SiO}_2$  being formed on the Si wafer surface through the dry etching to be employed in the treatment method of the present invention;

FIG. 3 is a plan view of the Si wafer showing the condition of the etching remaining through the etching operation when the air bubbles have been attached on the Si wafer;

FIG. 5 is a schematic view showing the sectional shape of the groove when the groove has been formed through the dry etching in the treatment method of the present invention; and

FIG. 6 is a schematic view showing the sectional shape of the groove when the wet etching has been performed with mixed acid.

#### DETAILED DESCRIPTION OF THE INVENTION

Before the description of the present invention proceeds, it is to be noted that like parts are designated by like reference numerals throughout the accompanying drawings.

#### EMBODIMENT 1

Referring now to the drawings, there is shown in FIG. 1, an etching apparatus of Si wafer according to a first embodiment of the present invention, which includes isopropanol 1 as liquid soluble with treatment liquid 2, the treatment liquid 2 employed as an etching liquid for Si wafer, rinsing water 3, a retaining jig 4 (hereinafter referred to as hanger) for Si wafer, the Si wafer 5 as a substrate to be treated, an exhaust port 6 for evacuating gaseous isopropanol or fluorine, and a drain port 7 for draining overflowed water 3. With the above, the experimental, practical method according to the embodiment of the present invention will be described in detailed hereinafter. Hot  $\text{SiO}_2$  films of 3000 Å, 10,000 Å and 20,000 Å are formed through the various period of treatment time by a pyrogenic method on the face of the Si wafer 5 having a diameter of 5 inches and sliced by the crystalline face of (1, 0, 0). Thereafter, the photoresistance is applied on the face of Si wafer 5 in the thickness of 1.2  $\mu\text{m}$  so that many line-shaped patterns lack being 1.5  $\mu\text{m}$  in width, 0.5 in length, separated by 5  $\mu\text{m}$  are developed on the entire Si wafer 5. The Si wafer 5 is dry-etched in  $\text{SiO}_2$  film by the use of the mixed gas (pressure 700 m Torr) between  $\text{CHF}_3$  and  $\text{C}_2\text{F}_6$ . Thereafter, the photoresistances are removed by the resistance ascha of the oxygen plasma. According to the observation by a microscope, the Si wafer 5, even in the Si wafer of any film thickness, provides at this time a hydrophilic  $\text{SiO}_2$  pattern 22 formed in the rectilinear shape on the hydrophobic Si monocrystal 21 as shown in FIG. 2.

On the other hand, the etching liquid 2 of  $\text{SiO}_2$  including fluoric acid and water having a mixing ratio of 1:200 as treatment liquid of the Si wafer 5, and the isopropanol having surface tension of 22.9 dyne/cm as liquid soluble with the etching liquid are put separately into a cell in the etching apparatus shown in FIG. 1. It is to be noted that the isopropanol is normally circulated by a bellows pump and filtered by the filter (0.1  $\mu\text{m}$ ) made of fluorine-resin film (not shown). Pure water 3 having specific resistance value of 18 M $\Omega$ -cm as the rinsing water is overflowed from the cell top-portion, normally flowing.

After the Si wafers 5 formed in the pattern are retained one by one by the hanger 4 and are quietly dipped in the isopropanol 1 for three minutes, they are pulled up from the isopropanol and are dipped in the etching liquid 2 for five minutes. According to the visual observation of the surfaces of the Si wafer 5 from the tower upper portion while the Si wafer 5 is dipped in the etching liquid, no air bubbles are attached on the Si wafers 5 of the film thickness. The Si wafers whose etching is finished are spin-dried after the sufficient washing operation with the pure water 3.

According to the microscope observation of the Si wafers 5, whose treatment operation is completed, the  $\text{SiO}_2$  film is etched and is made smaller in film thickness and width even in any Si wafer pattern, with no unevenness on the patterns.

On the other hand, as a first comparison embodiment for comparison, the Si wafer 5 provides the pattern of the SiO<sub>2</sub> film formed through the dry etching to remove the resistance. Then, the Si wafer is quietly dipped in etching liquid 2 directly without being dipped in the isopropanol 1. According to the observation the surfaces of the Si wafer 5 from the upper portion of the cell, several air bubbles are observed on the surface of the Si wafer 5. The Si wafer 5 is dipped for five minutes in the etching liquid 2, thereafter is dipped sufficiently in pure water 3, and is spin-dried. Then, according to the microscope observation of the surface of the Si wafer 5, the rectilinear pattern is out of shape, the pattern is recognized in which the convex portion 23 non-etched is provided on the end face of SiO<sub>2</sub> film. The SiO<sub>2</sub> films are observed particularly in the Si wafer 5 of 10,000 Å and 20,000 Å. This is because the air bubbles are attached when the Si wafer 5 is dipped in the etching liquid 2, and the bubble-attached locations remain without being etched.

Also, the similar experiments are performed even about n-propanol having surface tension of 25.3 dyne/cm, methanol having surface tension of 24.0 dyne/cm, ethanol having surface tension of 24.1 dyne/cm, acetic acid having surface tension of 29.6 dyne/cm, acetone having surface tension of 26.3 dyne/cm, acetic methyl having surface tension of 28 dyne/cm, methyl ethyl ketone having surface tension of 26.8 dyne/cm, instead of isopropanol as liquid soluble with treatment liquid, but the convex portion 23 non-etched of FIG. 3 is not observed. (The mixing ratio of each liquid is defined by volume ratio.)

The material soluble with the treatment liquid to be used in the present embodiment is required to be properly selected in accordance with the type of the treatment, the properties of the substrate to be treated, the nature of the treatment liquid or the like. As the water treatment liquid is mainly used in the washing or the etching of the Si wafer, alcohols such as methanol, ethanol, n-propanol, isopropanol, glycol and so on, ketones such as acetone and so on, carboxylic-acid such as acetic acid and so on, esters such as methyl acetate, ethyl acetate and so on, amines such as ethyl amine and so on, further sulfonic acid, electro-kinetic activator or the like, including the above-described materials used, are provided as the material soluble with the treatment liquid to be used. However, in the present invention, the simple substances or mixtures of any substance among them may be used. The methanol, ethanol, ethyl amine, acetic acid, methyl acetate, ethyl acetate, acetone, isopropanol, n-propanol or the like which is small in adsorption ability into the Si wafer, is likely to be displaced by the treatment liquid, and is 30 dyne/cm or smaller in surface tension.

These materials have a hydrophilic group of 13 OH, <O, —COOH, —COO—, SO<sub>3</sub>H or the like and a hydrophobic alkyl group within the molecule. When the Si wafer is exposed to the liquid or the steam (gas), the hydrophilic group is preferentially adhered on the hydrophilic portion of the Si wafer, the hydrophobic group is preferentially adhered on the hydrophobic portion of the Si wafer to form an accumulation film so that the entire Si wafer is likely to get wet with the hydrophilic treatment liquid or lipophilic treatment liquid. Also, as these materials are soluble with the treatment liquid such as water, they are dissolved in the treatment liquid during the treatment, and are decomposed in the treatment liquid. Furthermore, the air bub-

bles are likely to be disconnected from the compound of 30 dyne/cm or less in surface tension with no air bubbles remaining on the Si wafer surface. Thus, the uniform treatment may be performed without the air bubbles attached on the Si wafer so that the Si surface is not polluted.

Furthermore, a method of dipping the Si wafer in the liquid material, a method of jetting and spraying the liquid material from the nozzles or the like onto the Si wafer retained horizontal or vertical, a method of heating the material soluble with the treatment liquid, or applying ultrasonic waves producing gas to expose the Si wafer to the atmosphere, or other methods are available as a method of exposing the Si wafer to the material soluble with the treatment liquid. In the present invention, any method may be used. The dipping method is more preferable, because the apparatus is simple and the risk of the gas explosion is small.

Also, a method of dipping the Si wafer in the pure water or jetting the pure water in a shower condition to perform the washing operation is generally used as a method of removing the treatment liquid attached on the Si wafer. In order to increase the washing effect, the functions of oscillating the Si wafer, causing the bubbling of the ultrasonic waves or the gas in the rinsing cell, or rapidly exchanging the rinsing water are added. In the present invention, any method may be used or the combination of a plurality of methods from them may be used. The present invention may use any method of spin drying, steam drying, blow-off drying or the like as the method of drying the Si wafer, or may use the combined method.

The above method of the present invention can be applied to the same treating performance even in the sheet-number treatment or the patch treatment independently of the number of the sheets to be treated.

## EMBODIMENT 2

The second embodiment of the present invention will be described hereinafter.

The isopropanol placed in the glass beaker is dipped in the water bath heated to 100° C. to heat the isopropanol to 70° C. Thereafter, the glass beaker with the isopropanol in it is placed in a covered desiccator. The desiccator is filled with the steam of the isopropanol.

On the other hand, in the first embodiment, the pattern of the SiO<sub>2</sub> film is formed through the dry etching and the resistances are removed. Thereafter, the Si wafer 5 of 10,000 Å in SiO<sub>2</sub> film thickness is quietly placed for thirty minutes in the desiccator filled with the isopropanol steam, and is exposed to the isopropanol steam. The Si wafer 5 is retained by the hanger 4 of the etching apparatus used in the first embodiment, is dipped for five minutes in the etching liquid 2 including fluoric acid and water with a mixing ratio of 1:200, is washed with the pure water 3, thereafter is spin dried. The pattern of the Si wafer 5 is examined after the drying operation as in the first embodiment, but unevenness caused by a non-etched portion of the SiO<sub>2</sub> pattern does not exist.

Also, the same experiments are performed with the methanol, ethanol as the liquid soluble with the treatment liquid, thus showing the same results.

## EMBODIMENT 3

The third embodiment will be described hereinafter. The mixed liquid between ethanol and acetic acid, (for example, with mixing ratios of ethanol to acetic acid

being 6:4, 5:5 and 4:6), the mixed liquid between the ethanol and the water (for instance, with mixing ratios of ethanol to water being 8:2, 6:4, 5:5 and 4:6), the mixed liquid between the acetic acid and the water (for instance, with mixing ratios of acetic acid to water being 8:2, 6:4, 5:5 and 4:6), the mixed liquid between isopropyl alcohol and water, for instance, with mixing ratios being 6:4, 5:5 and 4:6, and the mixed liquid of 1:1 between the isopropyl alcohol and ethanol are used as the liquid soluble with the treatment liquid on the etching apparatus used in the first embodiment. The pattern is examined after the etching, washing and drying as in the first embodiment, and uneven surfaces caused by a non-etched portion remaining are not recognized.

Furthermore, the RCA washing liquid ( $\text{NH}_4\text{OH} \cdot \text{H}_2\text{O} = 1:2:7$ ; volume ratio,  $80^\circ \text{C}$ .) instead of the etching liquid in the first embodiment, and the isopropanol, methanol, ethanol as the liquid soluble with the RCA washing liquid, and the various kinds of mixed liquid are used to form the rectilinear  $\text{SiO}_2$  pattern on the Si base plate in the method similar to that of the embodiment 1. The Si wafer is dipped for three minutes in the above-described liquid soluble with the RCA washing liquid, thereafter is dipped for ten minutes in the RCA washing liquid. Thereafter, the Si wafer is sufficiently washed with water, is dried, and the surface is observed, by SEM (scanning type electronic microscope), for foreign materials attached on the Si wafer surface. Five through ten foreign materials (per fifty linear patterns) are sparsely recognized independently of the unevenness on the Si wafer surfaces. A large difference is not caused in the condition of the foreign-material attached due to the differences among the liquids soluble with the RCA washing liquid.

The Si wafer is directly dipped in the RCA washing liquid without being dipped in the liquid soluble with the RCA washing liquid, is washed, water-washed, dried. Thereafter, according to the observation of the Si wafer surface by the SEM, comparatively more foreign materials are recognized on the contact portion between the side face of the linear pattern 22 of the  $\text{SiO}_2$  and the Si crystal face 21, and a group of large foreign materials are confirmed to be located in places.

#### EMBODIMENT 4

The fourth embodiment of the present invention will be described hereinafter with reference to the drawings.

There is shown in FIG. 4, a container in section provided with a rotary pump 113 as means for reducing the pressure therein in the fourth embodiment of the present invention, which includes a container 111, a cell 112 for having the treatment liquid therein, a vacuum pump 113 as means for reducing the pressure, a stand 114 for having the Si wafer mounted thereon (hereinafter referred to as hanger), treatment liquid 115, a valve 116, an Si wafer as the substrate to be treated.

The  $\text{SiO}_2$  film of 10,000 Å is formed by the pyrogenic method on the Si wafer (5 inches in diameter), whose surfaces are finished into mirror face through the slicing operation with the crystal face of (1, 0, 0), thereafter the photo-resistance is applied into the thickness of 1.2 μm. The line-shaped pattern of 100 μm in length, 0.5 μm through 4.0 μm in width (every 0.5 μm) is developed by plurality on the entire Si wafer.

Si wafer is etched in  $\text{SiO}_2$  by the dry etching (with gas to be used, for instance, mixed gas of  $\text{CHF}_3 + \text{C}_2\text{F}_6$  having pressure of 700 m Torr).

The Si wafer is etched further by the dry etching (with gas to be used, for instance, mixed gas of  $\text{CCl}_4 + \text{O}_2$  having pressure of 80 m Torr) into the various depths (hereinafter referred to as the depths of the groove) of 1, 3, 5, 7 μm in the Si monocrystal through the variation of the etching time. Thereafter, the photoresistances are removed by the oxygen plasma. To observe the cross-sectional shape of the etching portion at this time by an electronic microscope (hereinafter referred to as SEM), one portion of the Si wafer is broken by the pattern forming portion. The condition is shown in FIG. 5. The bottom portion where the Si mono-crystal is etched (hereinafter referred to as groove) is made V in shape.

The Si wafer, whose groove depth is etched by 5 μm is placed into the hanger of FIG. 4, the mixed acid between the fluoric acid and nitric acid ( $\text{HF}:\text{HNO}_3 = 3:97$  (volume ratio), hereinafter referred to as mixed acid) as treatment liquid is placed into the cell 112. Thereafter, the container 111 is sealed, the hanger 114 is thrust in so that the Si wafer 117 is sunk completely into the mixed acid 115. Thereafter, the pressure within the container 111 is immediately reduced down to 30 Torr ( $15^\circ \text{C}$ . at the liquid temperature of the mixed acid 115) by the use of the rotary pump 113. Thereafter, the hanger 114 is vibrated several times from the outside of the decompression container 117, the valve 116 is opened to introduce the air into the container 111 to restore the pressure to the atmospheric pressure. After the lapse of 15 minutes from the dipping of the Si wafer 117 in the mixed acid 115 it is removed from the hanger 114 with a pincette. Immediately the Si wafer is washed with a large amount of superpure water having specific resistance value of 18 MΩ-cm, and, thereafter, is spin-dried at 5000 rpm. The etching is performed in the same manner even about the other Si wafers each being different in the groove depth. According to the observation of the Si wafer by the SEM, the side wall of the groove is uniformly etched with mixed acid to extend the groove width even in any pattern different in the groove width and the groove depth as shown in FIG. 6, with the groove bottom portion being changed to have such round shape from the V-shape like in FIG. 6. The mixed acid which is the wet etching treatment liquid of the Si wafer is penetrated into the entire groove so that the uniform treatment can be performed. Also, although many grooves are observed in the same manner across the entire Si wafer faces, the result is completely the same. Also, although the similar experiments are performed respectively at 50, 70, 100, 150 Torr, the results are the same.

On the other hand, the Si wafer is etched with the mixed acid without the pressure reduction within the container 111 with the use of the treatment apparatus shown in the fourth embodiment as a second comparison embodiment for comparison, by the method completely the same as that of the fourth embodiment in the other processes. It is found by the SEM observation (hereinafter referred to as the second comparison embodiment) that the portions where the interior portion of the groove is etched to extend the groove width are mixed with the portions where the groove width is not extended without the etching operation so as to cause the unevenness within the groove to make the etching unequal although the groove is etched with the mixed acid near the entrance thereof to extend the groove width even in any Si wafer different in the groove width and depth.

The operation of the treatment method in the above-described fourth embodiment will be described hereinafter.

The Si wafer which is the substrate to be treated is brought into contact against the treatment liquid within the container for decreasing the pressure therein. The pressure within the container is restored again to the atmospheric pressure after the pressure inside the container is reduced. The air bubbles which remain within the small unevenness on the Si wafer surface and are large enough to exert harmful influences upon the treatment are inflated to a large extent in the treatment liquid to disconnect them from the Si wafer surface through buoyancy.

Accordingly, the air bubbles do not prevent the concaved inner face of the Si wafer surface from coming into contact against the treatment liquid. The treatment liquid may be poured deep into the rear of the indentation by the atmospheric pressure if it may be different in size, thus resulting in uniform treatment (the thickness of the Si wafer of 5 inches in diameter with respect to the atmospheric pressure of 760 mm Hg' is 0.5 through 0.6 mm).

Also, the corrosion of the pressure-decreasing apparatus does not progress in the third treatment process of the conventional art even if the corrosive gas is caused, thus resulting in longer service life, because the pressure decreasing operation is temporarily performed.

Furthermore, the treatment method of the fourth embodiment has effects of applying the mechanical vibrations on the Si wafer, performing oscillations, and taking the Si wafer out of the treatment liquid for short time during the pressure reduction or stirring the treatment liquid by a pump, stirrer, ultrasonic waves or the like so as to disconnect the air bubbles as soon as possible.

#### EMBODIMENT 5

A fifth embodiment of the present invention will be described hereinafter.

In the fifth embodiment of the present invention, the RCA washing liquid including  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  in a mixing volume ratio of 1:2:7 at 80° C., instead of the mixed acid for wet etching in the fourth embodiment, is used. In the other processes, the Si wafer is etched, washed with water, dried in the completely same manner as in the fourth embodiment. The number of particle-shaped foreign materials on the side wall of the groove is observed by the SEM.

Also, the above-described RCA washing liquid, instead of the mixed acid in the second comparison embodiment is used for comparison. The number of the particle-shaped foreign materials on the groove side-walls (hereinafter referred to as the third comparison embodiment) is counted in the same manner as that of the second comparison embodiment. The counted number of the particle-shaped foreign materials in the fifth embodiment and the third comparison embodiment will be shown in the following Table 1.

It is to be noted that the counted value of Table 1 is the total of the foreign materials each being 0.3  $\mu\text{m}$  or more in diameter among the fifth line-shaped grooves, which are of 1.5  $\mu\text{m}$  in width, 100  $\mu\text{m}$  in length, respectively. It may be found from the results that the treatment operation may be performed with the washing liquid down to the bottom of the deep concave portion by the use of the treatment method of the present invention.

TABLE 1

Method of Washing Si Wafer	Number of Particles On Groove Side Wall
Fifth Embodiment	7
Third Embodiment	30

#### EMBODIMENT 6

A sixth embodiment of the present invention will be described hereinafter.

In the sixth embodiment of the present invention, the line-shaped groove is formed on the Si wafer through the dry etching as in the fourth embodiment. The Si wafer is set in the hanger 114 shown in FIG. 4. Thereafter, the water which is liquid soluble with the mixed acid is put into the cell 112 to seal the pressure decreasing container 111. The hanger 114 is thrust in. The wafer 117 is dipped in the water. Then, the pressure-decreasing container is reduced inside as low as 20 Torr (15° C. at the low temperature) by a vacuum pump 113. Also, the hanger 114 is rotated in the pressure-decreased condition by four times or five times at the angle of about 45°. Thereafter, the valve is opened to restore the pressure of the decompression apparatus to the atmospheric pressure. Thereafter, the Si wafer is dipped in the mixed acid, is etched, washed with water and dried. According to the observation of the groove-shaped pattern portion by the SEM, the groove-bottom portion is changed into the round V-shape as in FIG. 6, also the side wall of the groove is uniformly wet-etched, and can be uniformly treated as in the fourth embodiment.

On the other hand, by the use of the apparatus shown in the sixth embodiment for comparison, the pressure within the decompression container 111 is not decreased, but the Si wafer is etched in the mixed acid in completely the same method as in the fifth embodiment. According to the SEM observation (hereinafter referred to as the fourth comparison embodiment), the groove is etched near the entrance thereof to extend the groove width even in any Si wafer different in the groove depth. However, the interior of the groove can be treated only in the unequal way as in the second comparison embodiment.

#### EMBODIMENT 7

A seventh embodiment of the present invention will be described hereinafter.

Methanol having surface tension of 24 dyne/cm, ethanol having surface tension of 24.1 dyne/cm, n-propyl alcohol and isopropyl alcohol having surface tension of 22.9 dyne/cm, acetone having surface tension of 26.3 dyne/cm, and methyl ethyl ketone having surface tension of 26.8 dyne/cm, acetic acid having surface tension of 29.6 dyne/cm, in methyl acetate, ethyl acetate and nonionic series interfacial activator diluted to 0.5% with water, mixture of 1:1 between ethanol and acetic acid, mixed liquid between ethanol and water at a mixing ratio of either 6:4 or 4:6, the mixed liquid between acetic acid and water at a mixing ratio of either 6:4 or 4:6 are used as the liquid soluble with the mixed acid which is the wet etching agent of the Si wafer. The wet etching is performed as in the sixth embodiment so that the groove bottom portion is changed into the round V-shaped likewise and the mixed acid for etching use is penetrated through the entire groove. Also, the similar examinations are performed with the use of the

mixed liquid between methanol and water, isopropyl alcohol and water, or acetic acid and water, with the results being completely the same.

#### EMBODIMENT 8

An eighth embodiment of the present invention will be described hereinafter.

In the eighth embodiment of the present invention, the RCA washing liquid including  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  at a ratio of 1:2:7, at  $80^\circ\text{C}$ ., instead of the mixed acid for the wet etching in the sixth embodiment, is used. In the other processes, the Si wafer is etched, washed with water and dried in completely the same manner as in the sixth embodiment. The number of particle-shaped foreign materials on the side wall of the groove is observed by the SEM.

Also, the above-described RCA washing liquid, instead of the mixed acid in the fourth comparison embodiment, is used for comparison. The number of the particle shaped foreign materials on the groove side walls (hereinafter referred to as the fifth comparison embodiment) is counted in the same manner as that in the fourth embodiment. The counted number of the particle-shaped foreign materials in the eighth embodiment and the fifth comparison embodiment will be shown in the following Table 2.

It is to be noted that the counted value of Table 2 is the total of the foreign materials each being  $0.3\text{ }\mu\text{m}$  or more in diameter among the fifty line-shaped grooves, which are of  $1.5\text{ }\mu\text{m}$  in width,  $100\text{ }\mu\text{m}$  in length respectively.

It may be found from the results that the treatment operation may be performed with the washing liquid down to the bottom of the deep concave portion by the use of the treatment method of the eighth embodiment.

It is to be noted that each of the above-described embodiments shows only the examples of the wet etching and the washing process of the Si wafer. The present invention may be applied not only to the examples, but also to all the processes of treating, with the use of the treatment liquid, a substrate which is shaped like a plate and has unevenness on the surfaces.

TABLE 2

Method of Washing Si Wafer	Number of Particle-shaped Foreign Materials on Groove Side Wall
Eighth Embodiment	7
Fifth Embodiment	35

In the treatment method of Embodiment 6 through Embodiment 8, the liquid which is soluble with such treatment liquid as described hereinabove is contacted with the surface of the substrate to be treated, thereafter the pressure in the container is reduced, then the pressure is restored to atmospheric pressure, and the large air bubbles in the concave portion are inflated by the decompression, are removed with buoyancy, and the liquid is gradually penetrated into the surface between the very few small air bubbles remaining on the surface of the substrate to permit the entire surfaces of the substrate to be wetted with the treatment liquid. It is possible for the interior of the decompression container to be made completely vacuum. The degree of vacuum increases only up to the steam pressure when the liquid exists with the decompression container. For example, it is about 20 Torr at  $20^\circ\text{C}$  in the case of water. Accordingly, the air which is originally located in the concave portion of the substrate may be mostly re-

moved by the decompression de-airing operation, but air in an amount equivalent to 20/760 of the volume of the concave portion remains as it is.

The decompression degree of the treating method in the sixth through the eighth embodiments is determined by the steam pressure of the treatment liquid. The vacuum arrival degree is up to about 20 Torr at  $20^\circ\text{C}$  in the diluted liquid through the fluoric-acid water, the effective vacuum degree is within the range of 150 through 20 Torr ( $20^\circ\text{C}$ ), preferably 40 through 20 Torr.

The various pumps such as rotary pump, diffusion pump, mechanical booster pump, water seal pump and so on which are generally used as vacuum pumps are provided as apparatuses for decreasing the pressure within the container. In the present invention, any pump may be used, and a plurality of combinations from among them may be used.

#### EMBODIMENT 9

A ninth embodiment of the present invention will be described hereinafter with reference to the drawings.

In sample and the apparatus used in the present embodiment are the same as those manufactured and used in the fourth embodiment. The line-shaped pattern of  $100\text{ }\mu\text{m}$  in length, every  $0.5\text{ }\mu\text{m}$  in width (or there may be employed a value of  $0.5$  through  $4.0\text{ }\mu\text{m}$  in width), and 1, 3, 5, 7  $\mu\text{m}$  in depth is formed on the surface, and, thereafter, the photoresistance is removed. The Si wafer like this is used. The treatment apparatus of FIG. 4, which is the same as that of the fourth embodiment, is used.

The Si wafer, whose groove depth is etched by  $5\text{ }\mu\text{m}$  is placed into the hanger of FIG. 4, the mixed acid between the fluoric acid and the nitric acid ( $\text{HF}:\text{HNO}_3$ ) in a mixing volume ratio of 3 to 97 (hereinafter referred to as a mixed acid) as treatment liquid is placed into the cell 112. Thereafter, the container 111 is sealed, the pressure within the container 111 is reduced to 30 Torr at  $15^\circ\text{C}$  of the liquid temperature of the mixed acid 115 by the use of the rotary pump 113. Then, the hanger 114 is thrust in so that the Si wafer 117 is sunk completely into the mixed acid 115. Thereafter, the valve 116 is opened to introduce the air into the container 111 to restore the pressure to the atmospheric pressure. After the lapse of 15 minutes from the dipping of the Si wafer 117 in the mixed acid 115, the Si wafer 117 is lifted from the mixed acid 115 to take it out from the hanger 114 with a pincette. Immediately, the Si wafer is washed with a large amount of super-pure water having specific resistance value of  $18\text{ M}\Omega\text{-cm}$ , and thereafter, is spindried at 5000 rpm. The etching is performed in the same manner even about the other Si wafers each being different in the groove depth.

According to the observation of the Si wafer by the SEM, the side wall of the groove is uniformly etched with mixed acid to extend the groove width even in any pattern different in the groove width and the groove depth as shown in FIG. 6, with the groove bottom portion being changed to have such round shape as in FIG. 6 from the V-shape. The mixed acid which is wet etching treatment liquid of the Si wafer is penetrated into the entire groove so that the uniform treatment can be performed. Also, although many grooves are observed in the same manner across the entire Si wafer faces, the result is completely the same. Also, although



the similar experiments are performed respectively at 50, 70, 100, 150 Torr, the results are the same.

On the other hand, the Si wafer is etched with the mixed acid without the pressure reduction within the container 111 with the use of the apparatus shown in the fourth embodiment for comparison by the method which is completely the same method as that of the ninth embodiment in the other processes. It is found by the SEM observation (hereinafter referred to as the fifth comparison embodiment) that the portions where the interior portion of the groove is etched to extend the groove width are mixed with the portions where the groove width is not extended without the etching operation so as to cause the unevenness within the groove to make the etching unequal although the groove is etched with the mixed acid near the entrance thereof to extend the groove width even in any Si wafer different in the groove width and depth.

#### EMBODIMENT 10

A tenth embodiment of the present invention will be described hereinafter.

In the tenth embodiment of the present invention, the RCA washing liquid including  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$  in a volume ratio of 1:2:7 at 80° C., instead of the mixed acid for the wet etching use in the ninth embodiment, was used. In the other processes, the Si wafer is etched, washed with water, dried in the completely same manner as in the ninth embodiment. The number of particle-shaped foreign materials on the side wall of the groove is observed by the SEM.

Also, the above-described RCA washing liquid, instead of mixed acid used in the ninth comparison embodiment is used for comparison. The number of the particle-shaped foreign materials on the groove side walls (hereinafter referred to as the sixth comparison embodiment) is counted in the same manner. The counted number of the particle-shaped foreign materials is the tenth embodiment and the sixth comparison embodiment will be shown in the following Table 3.

It is to be noted that the counted value of Table 3 is the total of the foreign materials each being 0.3  $\mu\text{m}$  or more in diameter among the fifty line-shaped grooves, which are of 1.5  $\mu\text{m}$  in width, 100  $\mu\text{m}$  in length, respectively.

It may be found from the results that the treatment operation may be performed with the washing liquid down to the bottom of the deep concave portion by the use of the treatment method of the present embodiment.

TABLE 3

Method of Washing Si Wafer	Number of Particles on Groove Side Wall
Tenth Embodiment	3
Sixth Embodiment	32

#### EMBODIMENT 11

An eleventh embodiment of the present invention will be described hereinafter.

In the eleventh embodiment of the present invention, the line-shaped groove is formed on the Si wafer through the dry etching as in the ninth embodiment. The Si wafer is set in the hanger 114 shown in FIG. 4. Thereafter, the water which is liquid soluble with the mixed acid is put into the cell 112 to seal the pressure-decreasing container 111. The pressure-decreasing container 111 is reduced inside as low as 20 Torr at 15° C.

of the low temperature, by a rotary vacuum pump 113. Then, the hanger 114 is rotated in the pressure-decreased condition by four times or five times at the angle of about 45°, where the hanger is thrust in, and the wafer 117 is dipped in the water. Thereafter, the valve is opened to restore the pressure of the decompression apparatus to the atmospheric pressure. Thereafter, the Si wafer is dipped in the mixed acid, is etched, washed with water and dried. According to the observation of the groove-shaped pattern portion by the SEM, the groove-bottom portion is changed into the round V-shape as in FIG. 6, also the side wall of the groove is uniformly wet-etched, and can be uniformly treated as in the ninth embodiment.

On the other hand, by the use of the apparatus shown in the eleventh embodiment for comparison, the pressure within the decompression container 111 is not decreased, in the other process steps the Si wafer is etched in the mixed acid in completely the same method as in the ninth embodiment. According to the SEM observation (hereinafter referred to as the seventh comparison embodiment), the groove is etched near the entrance thereof to extend the groove width even in any Si wafer different in the groove depth. However, the interior of the groove can be treated only in the unequal way as in the fifth comparison embodiment.

In the treatment method in the ninth through eleventh embodiments, the Si wafer and the treatment liquid are placed separately within the container provided with an apparatus for decreasing the pressure within the container, and the pressure within the container is decreased. Thus, the air on the wafer surfaces can be removed even if unevenness caused by fine or deep grooves exists. The Si wafer is brought into contact against the treatment liquid in this condition, thereafter the pressure is restored to the atmospheric pressure. Accordingly, the air bubbles do not prevent the concaved inner face of the Si wafer surface from coming into contact against the treatment liquid. The treatment liquid may be poured deep into the rear of the indentation by the atmospheric pressure if it may be different in size, thus resulting in uniform treatment. In this embodiment, the thickness of the Si wafer of 5 inches in diameter with respect to the atmospheric pressure 760 mmHg is 0.5 through 0.6 mm.

#### EMBODIMENT 12

A twelfth embodiment of the present invention will be described hereinafter.

In the treatment method of the twelfth embodiment of the present invention, the liquid soluble with the treatment liquid is brought into contact with the surface of the substrate to be treated under the decreased pressure, thereafter the pressure is restored to the atmospheric pressure. The liquid is gradually penetrated into the boundary between very few air bubbles remaining on the surfaces of the substrate so that the entire surface of the substrate may be wetted with the treatment liquid.

The concrete contents of the twelfth embodiment using the liquid will be described hereinafter. The kind of the liquid soluble with the treatment liquid to be used in the treatment method of the twelfth embodiment is the same as that used in the treatment method of the sixth through eighth embodiments, and the operation is also similar.

Methanol having surface tension of 24 dyne/cm, ethanol having surface tension of 24.1 dyne/cm, n-propyl alcohol and isopropyl alcohol having surface tension of 22.9 dyne/cm, acetone having surface tension of 26.3 dyne/cm, and methyl ethyl ketone having surface tension of 26.8 dyne/cm, acetic acid having surface tension of 29.6 dyne/cm, in methyl acetate, ethyl acetate and nonionic series interfacial activator diluted to 0.5% with water, mixture of 1:1 between ethanol and acetic acid, mixed liquid between ethanol and water at a ratio of either 6:4 or 4:6, the mixed liquid between acetic acid and water at a ratio of either 6:4 or 4:6 are used as the liquid soluble with the mixed acid which is the wet etching agent of the Si wafer. The wet etching is performed as in the eleventh embodiment so that the groove bottom portion is changed into the round V-shape likewise and the mixed acid for etching use is penetrated through the entire groove. Also, the similar examinations are performed with the use of the mixed liquid between methanol and water, isopropyl alcohol and water, or acetic acid and water, with the results being completely the same.

#### EMBODIMENT 13

A thirteenth embodiment of the present invention will be described hereinafter.

In the thirteenth embodiment of the present invention, the RCA washing liquid including  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}$  at a ratio of 1:2:7 at 80° C., instead of the mixed acid for wet etching use in the twelfth embodiment, is used. In the other processes, the Si wafer is etched, washed with water, dried in the completely same manner as in the twelfth embodiment. The number of particle-shaped foreign materials on the side wall of the groove is observed by the SEM.

Also, the above-described RCA washing liquid, instead of the mixed acid used in the seventh comparison embodiment is used for comparison. The number of the particle-shaped foreign materials on the groove side walls (hereinafter referred to as the eighth comparison embodiment) is counted in the same manner. The counted number of the particle-shaped foreign materials in the thirteenth embodiment and the eighth comparison embodiment will be shown in the following Table 4.

It is to be noted that the counted value of Table 4 is the total of the foreign materials each being 0.3  $\mu\text{m}$  or more in diameter among the fifty line-shaped grooves, which are of 1.5  $\mu\text{m}$  in width, 100  $\mu\text{m}$  in length, respectively. It may be found from the results that the treatment operation may be performed with the washing liquid down to the bottom of the deep concave portion by the use of the treatment method of the present invention.

TABLE 4

Method of Washing Si Wafer	Number of Particle-shaped Foreign Materials of Groove on Groove Side Wall
Thirteenth Embodiment	2
Eighth Comparison Embodiment	35

Although the present invention has been fully described by way of example with reference to the accompanying drawings, it is to be noted here that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the scope of the

present invention, they should be construed as being included therein.

What is claimed is:

1. A treating method for a plate-shaped substrate comprising the steps of exposing a substrate to be treated to liquid or gas material which is soluble with treatment liquid and has a hydrophilic base and a hydrophobic base within the molecule of itself, thereafter dipping the substrate in the treatment liquid to apply the treatment, then removing said treatment liquid from the treated substrate.

2. The treating method in accordance with claim 1, wherein the liquid or gas material soluble with said treatment liquid is isopropanol.

3. The treating method in accordance with claim 1, wherein the substrate is a base plate, for manufacturing semiconductor elements, having fine unevenness on the surfaces.

4. A treating method for a plate-shaped substrate comprising the steps of contacting a substrate to be treated with a treatment liquid within a container which is provided with means for reducing pressure within the container, thereafter reducing the pressure within said container and restoring the pressure to atmospheric pressure, and completing the treatment to remove said treatment liquid from the treated substrate.

5. The treating method in accordance with claim 4, wherein the substrate is a base plate, for manufacturing semiconductor elements, having fine unevenness on the surfaces.

6. The treatment method in accordance with claim 4, comprising the step of moving said substrate and the treatment liquid relative to each other while the substrate is dipped in the treatment liquid.

7. A treatment method for a plate-shaped substrate comprising the steps of contacting a substrate to be treated with a liquid which is soluble with a treatment liquid within a container provided with pressure reducing means, thereafter reducing pressure within said container and restoring the pressure to atmospheric pressure, then contacting the substrate with the treatment liquid, and completing the treatment to remove said treatment liquid from the treated substrate.

8. The treatment method in accordance with claim 7, wherein the liquid soluble with the treatment liquid is liquid containing a material having a hydrophilic base and a hydrophobic base within the molecule of itself and is at least of compound selected from compound soluble in water.

9. The treatment method in accordance with claim 7, wherein the substrate is an Si base plate, for manufacturing semiconductor elements, having fine unevenness on the surfaces.

10. The treatment method in accordance with claim 7, wherein the substrate and the treatment liquid are moved relative to each other while the substrate is being treated with the treatment liquid.

11. A treatment method for a plate-shaped substrate comprising the steps of separately placing a substrate to be treated and a treatment liquid within a container provided with means for reducing pressure within the container, thereafter contacting said substrate with said treatment liquid under reduced pressure and restoring the pressure within said container to atmospheric pressure, and completing the treatment to remove said treatment liquid from the treated substrate.

12. The treatment method in accordance with claim 11, wherein the substrate is a base plate, for manufactur-



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ing semiconductor elements, having fine unevenness on the surfaces.

13. The treatment method in accordance with claim 11, further comprising the step of moving the substrate by mechanical means while the substrate is dipped in the treatment liquid.

14. A treatment method for a plate-shaped substrate comprising the steps of separately placing a substrate to be treated and a liquid which is soluble with a treatment liquid in a container, reducing pressure within said container, contacting the substrate with the liquid soluble with said treatment liquid under the reduced pressure, thereafter restoring the pressure within said container to atmospheric pressure, then contacting the substrate

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with the treatment liquid, and thereafter removing said treatment liquid from the treated substrate.

15. The treatment method in accordance with claim 14, wherein the liquid soluble with the treatment liquid is liquid containing a material having a hydrophilic base and a hydrophobic base without the molecule of itself and is at least one compound selected from compounds soluble in the water.

16. The treatment method in accordance with claim 14, wherein the substrate is an Si base plate, for manufacturing semiconductor elements, having fine unevenness on the surfaces.

17. The treatment method in accordance with claim 14, further comprising the step of moving the substrate by mechanical means while the substrate is contacted with the treatment liquid.

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Detailed Description Text - DETX (5):

On the other hand, the etching liquid 2 of SiO.sub.2 including fluoric acid and water having a mixing ratio of 1:200 as treatment liquid of the Si wafer 5, and the isopropanol having surface tension of 22.9 dyne/cm as liquid soluble with the etching liquid are put separately into a cell in the etching apparatus shown in FIG. 1. It is to be noted that the isopropanol is normally circulated by a bellows pump and filtered by the filter (0.1 .mu.m) made of fluorine-resin film (not shown). Pure water 3 having specific resistance value of 18 M.OMEGA..multidot.cm as the rinsing water is overflowed from the cell top-portion, normally flowing.

Detailed Description Text - DETX (30):

The Si wafer, whose groove depth is etched by 5 .mu.m is placed into the hanger of FIG. 4, the mixed acid between the fluoric acid and nitric acid (HF:HNO.sub.3 =3:97 (volume ratio), hereinafter referred to as mixed acid) as treatment liquid is placed into the cell 112. Thereafter, the container 111 is sealed, the hanger 114 is thrust in so that the Si wafer

117 is sunk completely into the mixed acid 115. Thereafter, the pressure within the container 111 is immediately reduced down to 30 Torr (15.degree. C. at the liquid temperature of the mixed acid 115) by the use of the rotary pump 113. Thereafter, the hanger 114 is vibrated several times from the outside of the decompression container 117, the valve 116 is opened to introduce the air into the container 111 to restore the pressure to the atmospheric pressure. After the lapse of 15 minutes from the dipping of the Si wafer 117 in the mixed acid 115 it is removed from the hanger 114 with a pincette. Immediately the Si wafer is washed with a large amount of superpure water having specific resistance value of 18 M.OMEGA..multidot.cm, and, thereafter, is spin-dried at 5000 rpm. The etching is performed in the same manner even about the other Si wafers each being different in the groove depth. According to the observation of the Si wafer by the SEM, the side wall of the groove is uniformly etched with mixed acid to extend the groove width even in any pattern different in the groove width and the groove depth as shown in FIG. 6, with the groove bottom portion being changed to have such round shape from the V-shape like in FIG. 6. The mixed acid which is the wet etching treatment liquid of the Si wafer is penetrated into the entire groove so that the uniform treatment can be performed. Also, although many grooves are observed in the same manner across the entire Si wafer faces, the result is completely the same. Also, although the similar experiments are performed respectively at 50, 70, 100, 150 Torr, the results are the same.

Detailed Description Text - DETX (62):

The Si wafer, whose groove depth is etched by 5 .mu.m is

placed into the hanger of FIG. 4, the mixed acid between the fluororic acid and the nitric acid (HF:HNO<sub>3</sub>) in a mixing volume ratio of 3 to 97 (hereinafter referred to as a mixed acid) as treatment liquid is placed into the cell 112. Thereafter, the container 111 is sealed, the pressure within the container 111 is reduced to 30 Torr at 15.degree. C. of the liquid temperature of the mixed acid 115 by the use of the rotary pump 113. Then, the hanger 114 is thrust in so that the Si wafer 117 is sunk completely into the mixed acid 115. Thereafter, the valve 116 is opened to introduce the air into the container 111 to restore the pressure to the atmospheric pressure. After the lapse of 15 minutes from the dipping of the Si wafer 117 in the mixed acid 115, the Si wafer 117 is lifted from the mixed acid 115 to take it out from the hanger 114 with a pincette. Immediately, the Si wafer is washed with a large amount of super-pure water having specific resistance value of 18 M.OMEGA..multidot.cm, and thereafter, is spin-dried at 5000 rpm. The etching is performed in the same manner even about the other Si wafers each being different in the groove depth.